

AROMATIC POLYELECTROLYTES BASED ON
SULFONATED POLYBENZOBISTHAZOLES AND
SULFONATOPROPOXY-SUBSTITUTED POLY(*p*-PHENYLENES)

By

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I dedicate this dissertation to my parents and brother for their unending encouragement and support during my graduate work.

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Polyelectrolytes with aromatic backbones, specifically sulfonated polybenzothiazoles (PBTs), and sulfonatopropoxy-substituted poly(*p*-phenylenes) (PPPs), have been synthesized and characterized. Sulfonated PBTs (*p*-sulfo PBT, *m*-sulfo PBT, and *m*-disulfo PBT) have been synthesized using polycondensation of sulfo-substituted phthalic acids with 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) in a poly(phosphoric acid) (PPA) medium. The polymers have been characterized by ¹³C-NMR, FT-IR, elemental analysis, thermogravimetric analysis, and solution viscosity measurements. Structural analyses confirm the synthesis of *p*-sulfo PBT and *m*-disulfo PBT, but suggest that the sulfo groups of *m*-sulfo PBT are cleaved during the polymerization.

The addition of sulfo groups onto PBT resulted in an enhanced solubility in organic solvents, while *m*-disulfo PBT is water soluble at room temperature. A mixed solvent system of MSA and CH₂Cl₂ proved to be the most aggressive of solvents evaluated at room temperature. *p*-Sulfo PBT exhibited birefringence

in DMSO at concentrations of 5 to 10 w/w %, as well as in H₂O/DMSO at 3 w/w %, indicating the material to be lyotropic.

Water soluble poly(*p*-phenylene) derivatives, poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-1,4-phenylene] sodium salt (PPP-OPSO₃), and poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-4,4'-biphenylene] sodium salt (PPBP-OPSO₃), have been synthesized through a coupling reaction of 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene sodium salt with 1,4-benzene-diboronic acid, or 4,4'-biphenyldiboronic acid-(2,2'-dimethyl)propyldiester using a water soluble Pd(0) catalyst or Pd(OAc)₂. The pH dependence of the coupling reaction at pH levels of 8.0, 10.0, and 12.0 was investigated and resulted in pH independence at pH levels of 10.0 and 12.0. The λ_{max} of the π - π^* absorption for PPP-OPSO₃ is found at 339-342 nm, while that of PPBP-OPSO₃ showed a bathochromic shift to 349-352 nm. Fluorescence spectra of these polymers in solution indicate that the emission occurs at 410-430 nm causing these polymers to be blue emitters. Luminescence properties of PPP-OPSO₃/polyethyleneimine(PEI) multi-layers were investigated, showing blue photoluminescence and electroluminescence.

CHAPTER 1 INTRODUCTION

1-1 General Properties of Rigid-rod Polymers

Recently significant attention has been devoted to rigid-rod polymers which possess physical properties such as high temperature stability, nonflammability, and high chemical resistance. High modulus and high tensile strength fibers can be obtained through the spinning of polymer solutions of polybenzimidazoles (PBIs),¹ polybenzoxazoles (PBOs),^{2,3} or polybenzothiazoles (PBTs)^{2,4} (Figure 1-1). These properties prove these materials useful in such applications as thermal-protective clothing, and numerous other high temperature and chemical-resistant applications.

However, the early polymers were found to be somewhat intractable. The rigid-rod polymers were only soluble in strong protic acids such as chlorosulfonic acid, methanesulfonic acid (MSA), and sulfuric acid, making them difficult to process.¹⁻⁴ Aromatic PBIs with flexible units dissolve in organic solvents, such as dimethylacetamide (DMA), and have a water-absorbing capability. They are useful for such applications as fire-resistance textile fibers and membranes. On the other hand, PBTs are less useful than PBIs because of low processibility due to insolubility in organic solvents, although wholly aromatic PBTs are among the most thermally and thermooxidatively stable organic polymers known. The processing methods developed for PBTs originated from the discovery of lyotropic liquid crystallinity in rigid-rod polymer solutions. Many processing methods were subsequently developed to obtain excellent mechanical properties in fibers and films of PBTs. Composite

technology uses these polymers as reinforcements in blends with common polymers.

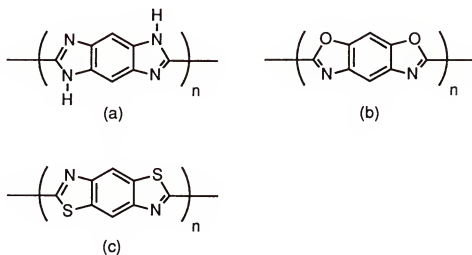


Figure 1-1 Examples of (a) polybenzimidazoles (PBIs), (b) polybenzoxazoles (PBOs), and (c) polybenzothiazoles (PBTs).

Poly(*p*-phenylenes) (PPPs) are of great interest for their potential role as high performance, electrically conducting, electroluminescent, and nonlinear optical materials. (Figure 1-2) However, the material properties of non-derivatized PPPs are poor due to their intractability.⁵ In many of the direct syntheses, the reaction conditions do not allow a regiospecific coupling reaction to occur. Furthermore, the precipitation of the polymers during polymerization stops increase of molecular weight leading to a low degree of polymerization.

In order to overcome the intractability of these polymers, structural modifications and the use of precursor polymers have been explored to improve processability. At the same time, considerable effort has been put forth to enhance the solubility of aromatic polymers through the derivatization of the pre-formed main chain, or the polymerization of substituted monomers.⁶⁻¹³

1-2 Derivatization of Polymers based on Aromatic Backbones

Previously, aromatic polyamides such as poly(*p*-phenyleneterephthalamide) (PPTA) were overlooked as substrates for grafting by aliphatic substituents because of low solubility and lack of softening or melting points.

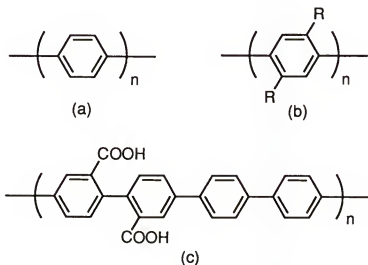
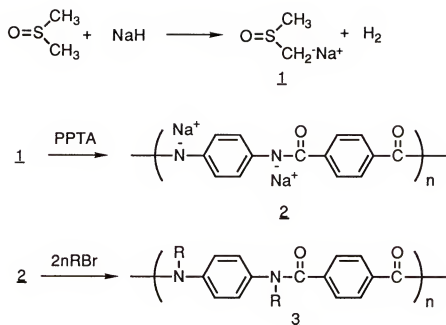


Figure 1-2 Examples of (a) unsubstituted PPP, (b) organic soluble PPP, and (c) water soluble PPP.

Takayanagi et al.⁶ first introduced a method for dissolving organic insoluble PPTA via metallation in a solution using a sodium methylsulfinylcarbanion-dimethylsulfoxide solvent at low temperatures. Since that time, several modifications of the PPTA polyanion have been made to produce organic soluble polymers (Figure 1-3). The introduction of aliphatic chains onto the amide groups of PPTA increased solubility but decreased thermal stability relative unsubstituted PPTA. Kashani et al.⁷ reported a similar preparation method by preparing graft copolymers of poly(*m*-phenylene isophthalamide) via metallation in a solution of sodium in liquid ammonia. However, the reaction is heterogeneous and the metallated centers are not equally accessible to the reactant. Therefore, uniform distribution of substituents throughout the product is very important. The preparation of graft copolymers of PPTA with acrylonitrile



where R = $-\text{C}_{18}\text{H}_{37}$, $-\text{CH}_2\text{COOH}$

or

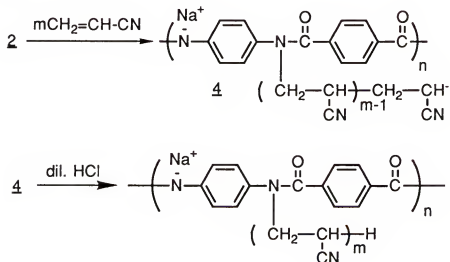


Figure 1-3 Scheme for the metallation of PPTA, and examples of N-alkylated and N-grafted PPTA.

using this method was successful. However, stoichiometric derivatization is difficult because of the decreased reactivity to deprotonation of the second N-H site at each repeat unit.

The attachment of ionic pendant groups onto pre-existing polymers in order to induce solubility in aqueous systems has been investigated.⁸⁻¹² Uno et al.⁸ synthesized polybibenzimidazole-based polyelectrolytes where the ionic groups are incorporated using sulfonated aromatic diacid monomers. Gieselman and Reynolds⁹ have also utilized the PPTA polyanion technique to synthesize water soluble PPTA derivatives carrying N-alkyl sulfonates. The stoichiometric derivatization of the PPTA backbones was difficult, as described above, and led to maximum substitution level of 66 % for N-alkylsulfonates.

Polybibenzimidazole-based polyelectrolytes were subsequently synthesized by attaching ionic pendant groups through the reaction of the deprotonated parent ion with 1,3-propane sultone or *p*-bromomethylbenzenesulfonate¹⁰ (Figure 1-4). Controlled derivatization was achieved in this instance, yielding a maximum substitution level of 39 % for N-*p*-methylenbenzenesulfonate and 99 % for N-propylsulfonates.

Dang and Arnold¹¹ also reported polybenzimidazole derivatives carrying sulfonatopropyl substituents. Bai et al.¹² derivatized sulfonated rigid-rod polybenzimidazole with sulfonatopropyl pendants, resulting in water solubility of those polymers. However, as pointed out above, stoichiometric derivatization is not easily achieved.

1-3 Introduction of Substituents onto the Polymer Repeat Unit through Polymerization

One method for producing structurally homogeneous polyelectrolytes is the polycondensation of ion containing monomers. The advantage of this method is the stoichiometric incorporation of ionic groups onto each repeat unit.

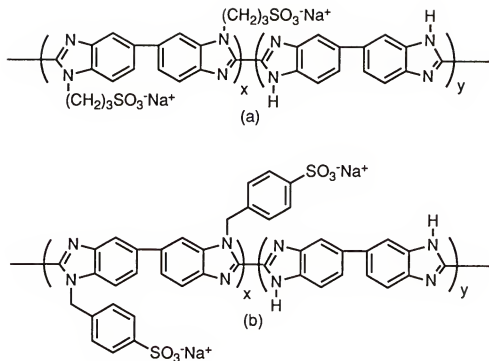


Figure 1-4 The structures of (a) N-sulfopropyl-substituted polybibenzimidazole and (b) N-*p*-sulfobenzyl-substituted polybibenzimidazole.

Vandenberg et al.¹³ prepared water soluble PPTA derivatives, poly[N,N'-(sulfo-*p*-phenylene)terephthalamide], by solution polymerization using 2,5-diaminobenzenesulfonic acid with terephthaloyl chloride (Figure 1-5).

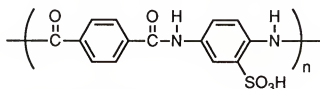


Figure 1-5 Structure of sulfonated PPTA.

The polymers obtained had a low molecular weight and were soluble at an elevated temperature (ca. 100 °C) in water as the free acid or as DMAc or pyridine salts.

Since the PBT synthesis was developed by Arnold et al., many substituted PBT derivatives have been reported. Among these, PBTs with methyl pendant groups,¹⁴ PBT with hydroxy pendant groups,¹⁵ and PBIs with

benzothiazolyl pendant groups^{16,17} on the *p*-phenylene ring are interesting (Figure 1-6). The introduction of pendant groups alters the polymer properties such as solubility, intrinsic viscosity, and thermal stability. Summarizing these results, the introduction of pendant groups generally the solubility of resultant PBTs increases while the intrinsic viscosity and thermal stability of these polymers decrease. Among them, dihydroxy-substituted PBT has the possibility of a pseudo-ladder structure due to intramolecular hydrogen bondings of hydroxy groups.

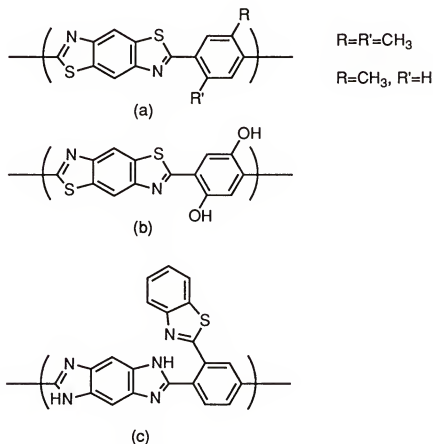


Figure 1-6 Examples of (a) PBT with methyl pendant groups, (b) PBT with hydroxy pendant groups, and (c) PBI with benzothiazolyl pendant groups.

1-4 Polybenzobisthiazoles and Their Properties

Among the variety of PBTs, poly(*p*-phenylenebenzobisthiazole) (*trans*-PBT) is unique due to its rigidity with essentially one rod-like conformation. Wolfe et al.^{2,4} reported the preparation of *trans*-PBT and its derivatives (Figure 1-7). These polymers were found to be highly thermally and thermooxidatively stable.

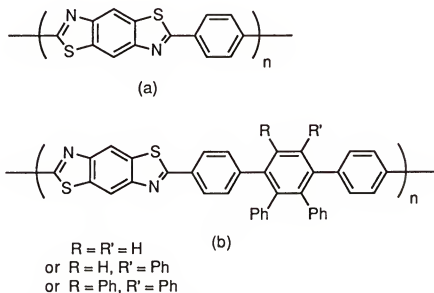


Figure 1-7 Structures of (a) *trans*-PBT and (b) PBT derivatives.

The high axial ratio of the individual molecules results in a low critical concentration for forming a liquid crystalline or nematic phase. For example, when syntheses of *trans*-PBTs were conducted at concentrations of 5-10 wt %, the polymeric mixtures became liquid crystalline, and intrinsic viscosities of the resultant polymers as high as 31 dL/g were obtained. Full chain extension is essential for maximizing the reinforcement imparted by these polymers in rigid-rod, molecular composite technology.

Melt condensation that relies on high temperature was attempted for the synthesis of PBTs.¹⁸ It was found that the monomers degraded at the high

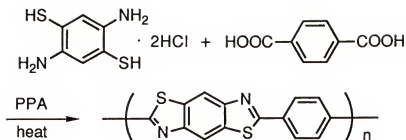
temperatures required for polymerization (ca. 210-330 °C) and solution polymerization is a better route to high polymer.

The synthesis of PBTs were successfully achieved using solution condensation in poly(phosphoric acid) (PPA). PPA is an excellent solvent for this polymerization because it is a non-oxidizing medium and is readily removed from the product during coagulation.¹⁹ PPA has sufficient acidity to maintain polymer solubility by protonating the heterocyclic rings of PBT. At the same time, the acidity is low enough to allow sufficient reactivity of the sulfur nucleophiles. PPA activates the carboxylic acid derivative toward an acyl carbonium ion by a phosphorylation mechanism^{2,20} (Figure 1-8).

As shown in Figure 1-8, PPA lowers activation temperatures of the carbonyl groups in aromatic acids to 165 °C.²⁰ By using PPA as a polymerization solvent, the achievable molecular weight depends on the polymer concentration during polymerization, and on P₂O₅ content in PPA during the final stage of polymerization. Results reported by Arnold et al.^{2,4} indicate that the highest molecular weight is obtained if the P₂O₅ content is higher than 83 % and if the polymerization is conducted in the nematic phase.

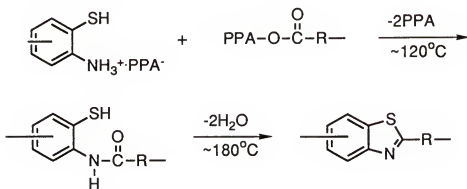
By polymerizing terephthalic acid with 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT), *trans*-PBT was prepared. *trans*-PBT has exocyclic bonds that are co-linear. The three condensed rings and the phenyl rings are coplanar with the heterocycles. However, the phenyl rings of *trans*-PBT are out of plane having a dihedral angle of ca. 23 °.

It was pointed out in Section 1-1 that rigid-rod PBTs have low processibility which provides less opportunity for use compared with aromatic nonrigid-rod PBIs because PBTs are insoluble in organic solvents. Several approaches to the solubilization of PBTs have been reported by means of



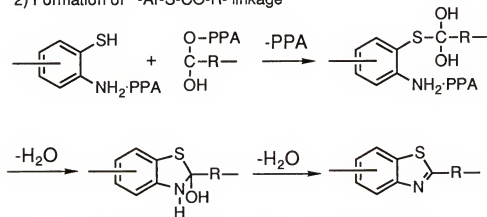
Two possible ring formation reactions

1) Formation of -Ar-NH-CO-R- linkage



Basis: formation of polyamide intermediate at a relatively low temperature.

2) Formation of -Ar-S-CO-R- linkage



Basis: the basicity of -SH is greater than that of -NH₂ in PPA

Figure 1-8 Scheme of PBT formation and two proposed routes for the ring formation.

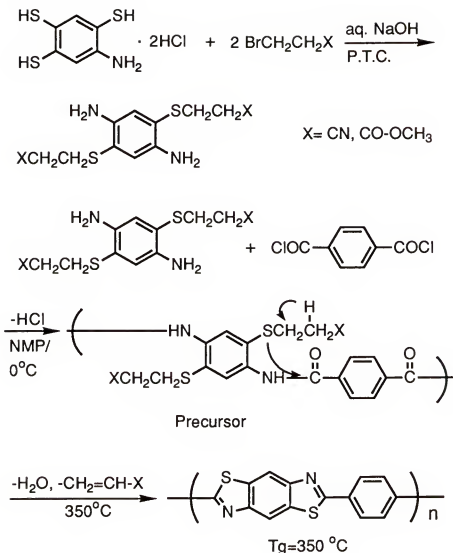


Figure 1-9 The structure of precursor and PBT ring formation route.

complex formation with Lewis acids in aprotic organic solvents.^{21,22} Hattari et al.²³ have reported a two step synthesis of PBTs via precursor polyamides from 2,5-bis(isopropylthio)-1,4-phenylenediamine and dicarboxylic acid chlorides (Figure 1-9), while Kricheldorf and Jahneke²⁴ has reported a trimethylsilyl-substituted precursor.

The aromatic polyamide precursors are soluble in organic solvents such as N,N-dimethylacetamide, N-methyl-2-pyrrolidone, dimethylsulfoxide, chloroform, and pyridine as well as strong acids such as MSA. The PBTs

obtained from the precursor polyamides showed good thermal properties which were comparable to those of the PBTs synthesized by solution polycondensation in PPA. Unfortunately, this work did not report intrinsic viscosity data of PBTs synthesized by this method. The precursor method may provide a new path for processing intractable PBTs.

1-5 Motivation for the Synthesis of Sulfo PBTs by the Introduction of Sulfonates onto the Repeat Units of PBTs

In order to improve processability of PBTs through improved solubility and modify the properties of the resultant fabricated specimens, Evers et al.²⁵ synthesized all-*para* PBTs by polycondensation of DABDT with reactive diphenoxybenzene monomer in PPA (Figure 1-10). However, the presence of the ether linkage resulted in decreased thermooxidative stability (ca. 316 °C) of the polymers compared to the *trans* PBTs (ca. 700 °C). At the same time, solubility was not improved in any solvents except strong acids such as MSA.

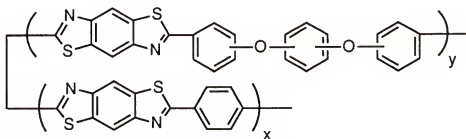


Figure 1-10 Structure of articulated all-*para* PBT.

With the background described above, the syntheses of fully *para* linked rigid-rod aromatic polyelectrolytes by introducing sulfonates onto *trans* PBT were targeted. PBTs dissolve only in strong acids. The sulfo groups introduced directly onto the PBT aromatic backbone may prove useful because of their ability to induce solubility in common solvents without a loss of rigidity. *Para* sulfo, *meta* sulfo, their copolymers, and *meta* disulfo PBTs have been synthesized and characterized throughout this work (Figure 1-11).

Solubility tests in protic acids, protic organic solvents, and water have been carried out to determine best solvent for these sulfonated polymers. Physical property changes were determined by means of intrinsic viscosity measurements of the polymers compared with unsubstituted PBT standard.

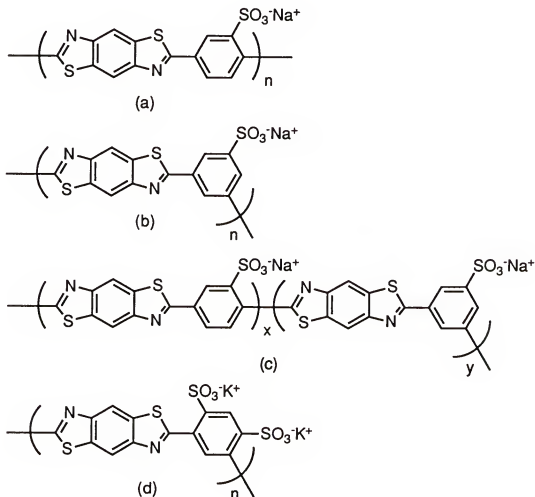


Figure 1-11 Structures of (a) *p*-sulfo PBT, (b) *m*-sulfo PBT, (c) their copolymer, and (d) *m*-disulfo PBT.

1-6 Synthesis of Poly(*p*-phenylene) (PPP) and Its Analogs

Along with the rigid-rod polymers introduced above, poly(*p*-phenylene) (PPP) and its derivatives have also been of great interest. PPPs are macromolecules comprised of benzenoid aromatic nuclei directly linked to one

another through the *para* position by C-C bonds.²⁶ Until 1979, the major interest in PPPs resulted from their excellent thermal and thermooxidative stabilities due to its rigidity. Continuing interest has developed from the possibility of transforming PPP from an electrical insulator into an electrical conductor upon doping with electron acceptors or donors.²⁷

PPP homopolymers prepared by oxidative cationic polymerization via treatment with various Lewis acid-oxidant systems (e.g. aluminum trichloride-cupric chloride) at mild temperatures were introduced by Speight et al.^{28(a)} and Kovacic and Jones^{28(b)} (Figure 1-12). The proposed mechanism of this reaction involves an initial one-electron oxidation of benzene to its radical cation, followed by propagation of the radical cation with several neutral benzene molecules in a progressive fashion.²⁹ Subsequently, a second one-electron oxidation followed by loss of two protons aromatizes the terminal rings.

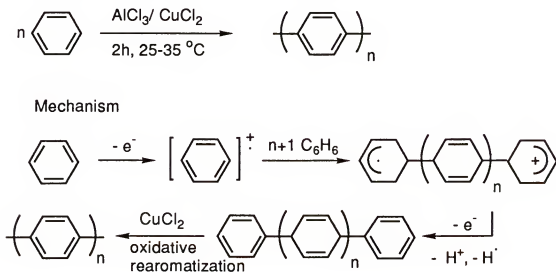


Figure 1-12 Structure of PPP synthesized by Kovacic's method and proposed mechanism for polymerization.

Oxidative rearomatization of the dihydro structures by cupric chloride gives PPP. Numerous other catalysts and oxidants were employed for the synthesis of PPP. Cu^{2+} and Ru^{2+} ion-exchanged montmorillonite clays,³⁰ and

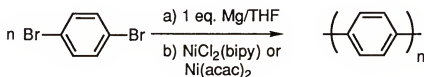
AsF₃/AsF₅³¹ are among the more novel reagents which convert benzene to PPP. AsF₃/AsF₅ yields a homogeneous solution of PPP and converts biphenyl and *p*-terphenyl to PPP.³² This reaction combines the polymerization step with a doping step to give conductive PPP directly. Polyphenylenes with *meta* linkages are obtained by treatment of *m*-terphenyl or a mixture of *m*-terphenyl and biphenyl with a Lewis acid-oxidant at temperatures of 85-180 °C.³³ The polyphenylenes with *meta* linkages are more processible.

Electrochemical oxidation of benzene in a two phase, HF-benzene system on a Pt electrode gives free-standing films of polyphenylene which contain *ortho*, *meta*, and *para* linkages.³⁴ Flexible, electrically conductive films of PPP are obtained through anodic oxidation of benzene in a nitrobenzene solution containing a composite electrolyte of CuCl₂ and LiAsF₆.³⁵ The product is structurally similar to chemically produced PPP, as determined by IR and elemental analyses. Also, anodic oxidation of benzene in BF₃-etherate gives flexible, highly conducting films of PPP.³⁶

A number of methods for the preparation of oligophenylenes and polyphenylenes involve the use of a metal mediated reaction. In the past, condensation of dihaloaromatics with copper (Ullmann reaction) or with alkali metals (Würtz-Fittig reaction) has been used extensively to prepare biphenyl or terphenyl species. However, these reactions suffer from deficiencies, such as low yield and significant formation of by-product, and have been used for the synthesis of oligomers with specific structures.

Of greater utility for PPP preparation is the coupling of Grignard reagents. PPP has been synthesized in good yield by coupling of the mono-Grignard reagent of *p*-dihalobenzene in the presence of nickel complex catalysts^{37,38} (Figure 1-13). The resulting product is lighter in color, but otherwise is similar in physical characteristics to PPP prepared using oxidative polymerization. In

general, the Grignard cross coupling reactions give higher yields and fewer side-products than from the corresponding Ullmann reactions.



Mechanism

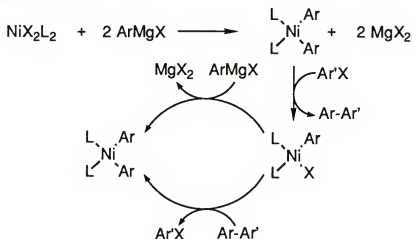


Figure 1-13 Scheme of PPP synthesis using Grignard with Ni complex catalyst and proposed mechanism.

Polymerization of 1,3-cyclohexadiene by treatment with various Ziegler type initiator systems or *n*-butyllithium affords poly(1,3-cyclohexadiene) with regular 1,4-linkages. Subsequent dehydrogenation with chloranil or halogenation/pyrolysis gives PPP³⁹ (Figure 1-14). Cationic polymerization of 1,3-cyclohexadiene produces a polymer with a mixture of 1,4- and 1,2-bonded structures, which is converted to a polyphenylene with *ortho* and *para* linkages. Diester derivatives of 5,6-dihydroxy-1,3-cyclohexadiene have been polymerized under radical conditions using benzoyl peroxide or AIBN and the resulting polycyclohexylenes converted to PPP by pyrolysis (Figure 1-15).

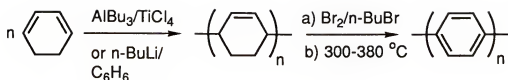


Figure 1-14 Scheme of PPP synthesis using Ziegler or anionic initiator.

Ballard et al.⁴⁰ synthesized a *cis*-diacetate derivative using bacterial oxidation of benzene by the genetically modified bacteria *Pseudomonas putida*. These materials are composed mainly of the 1,4-structure. Small amounts (less than 15 %) of the 1,2-structures are also present. Pyrolysis of the *cis*-diesters proceeds smoothly with the loss of both esters, resulting in aromatization of the polymer. However, NMR analysis indicated that complete aromatization does not occur during the thermal treatment.⁴¹

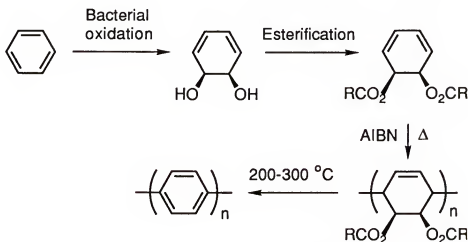


Figure 1-15 Scheme of PPP synthesis using radical initiator.

Unsubstituted PPP was also obtained from 1,4-cycloadditions of biscyclopentadienones or bispyrones with bisacetylenes⁴² (Figure 1-16). The polymer from cycloaddition is as insoluble in organic solvents as PPPs prepared by the other methods, but the resultant PPP is light yellow in color, as opposed to dark brown for the polymer synthesized by oxidative polymerization of benzene.

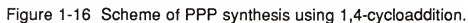

$$\begin{array}{c}
 n \text{ } ^+\text{N}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-N}_2^+ \xrightarrow[\Delta]{\text{CuCl, NH}_3} (\text{C}_6\text{H}_4)_n \\
 \text{(a)} \\
 n \text{ Br-C}_6\text{H}_4\text{-Br} + 2ne^- \xrightarrow[\text{b) NiCl}_2(\text{bipy}) \text{ or Ni(acac)}_2]{\text{a) 1 eq. Mg/THF}} (\text{C}_6\text{H}_4)_n + 2n\text{Br}^- \\
 \text{(b)}
 \end{array}$$

Figure 1-17 Scheme of PPP synthesis using (a) diazonium salt and (b) electrochemical reduction.

Electrochemical reduction of 1,4-dibromobenzene in THF/HMPA on a mercury pool electrode in the presence of Ni^0 complex catalysts and lithium perchlorate as the electrolyte gave good yields of insoluble PPP as a pale yellow powder.⁴⁴ (Figure 1-17 (b)) The Ni^0 complexes are generated *in situ* by

electrochemical reduction of NiX_2L_2 ($\text{X}=\text{Cl}$ or Br ; $\text{L}=\text{PPh}_3$ or $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$). The resulting electroactive coating is not likely to be of PPP since it was found to contain one Ni per six to seven phenylene moieties.

1-7 Synthetic Routes to Homoaromatic PPP and Its Derivatives

Most of the direct syntheses of PPP are carried out under severe conditions which do not allow a regiospecific coupling reaction to take place. Therefore, the formation of *ortho* or *meta* linkages, as well as *para* linkages between benzene rings, or cross-coupling occurs. The molecular weights achieved are also very low due to low solubility. Typical degrees of polymerization (X_n s) range from 5 to 15.⁵ The precursor approach achieved higher molecular weights than direct syntheses, as the precursor polymers retain a high degree of solubility. However, structural irregularities included in precursors are transferred into the final polyarylene and conversion of the precursor polymer to final product is not as clean as desired. Moreover, there are a limited number of precursor polymers available.

In 1978, Yamamoto et al.⁴⁵ reported the reaction between dihaloaromatic compounds and Mg metal in the presence of various low valent Ni catalysts. When 1,4-dibromobenzene, one equivalent of Mg, and Ni catalyst in refluxing in THF is used, an exclusively *para*-linked, low molecular weight PPP is obtained (Figure 1-18).

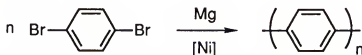


Figure 1-18 Scheme of PPP synthesis using Yamamoto coupling.

This reaction occurs under very mild conditions and average X_n ranges from 10-15. Termination of the Ni-catalyzed polycondensation can be a problem associated with insolubility of unsubstituted polymers due to

precipitation of the growing polymer chain at an early stage of growth. In order to solve this termination problem, monomers carrying flexible chains were employed. The attachment of these chains was believed to drastically increase the solubility of low molecular weight oligomers, as well as of the polymers,⁴⁶ and thus achieve higher average X_n . However, results showed that molecular weight could not be pushed beyond an average $X_n=15$ even though the resulting PPP had a perfect 1,4-connected structure.

Suzuki et al.⁴⁷ introduced the Pd-catalyzed coupling of various bromobenzene derivatives with benzene boronic acid and its cyclic esters. These cross-coupling reactions (Suzuki coupling), using less electropositive boron rather than magnesium, provide very good yields even in sterically demanding cases. One advantage of this coupling is that the influence of substituents attached at the *ortho* positions in the reaction was found to be negligible.

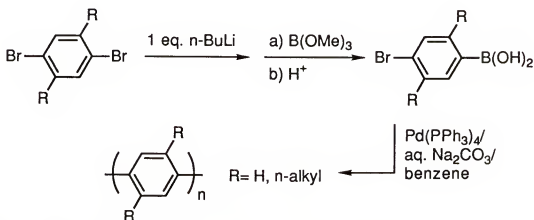


Figure 1-19 Scheme of PPP synthesis using Suzuki coupling.

Polymerization of 1,4-dibromobenzene with dialkyl substituents using a Suzuki coupling was carried out by Rehahn et al.⁴⁸ The conversion of one bromo-substituent to the boronic acid function was achieved by the reaction shown in Figure 1-19. The polymerization of an AB type monomer resulted in a

colorless and organic-soluble polymer whose molecular weight was higher than Yamamoto coupling methods. Due to the lack of an appropriate standard, the SEC traces could not be analyzed quantitatively. Vapor phase osmometry (VPO) measurement gave average $X_n=30$. One important advantage of Suzuki coupling is that the PPP generated is quite pure.

However, It cannot be overlooked that the attachment of flexible chains to the unsubstituted PPP changes its conformation. In the specific case of PPP, the dihedral angle between two adjacent phenyl rings will increase because of the steric interactions between the *ortho* hydrogens of adjacent rings. Large deviations from coplanarity may have a significant effect on electrical and optical properties.

1-8 PPP Derivatives and Homoaromatic Polyarylenes with Functional Groups

Recent research in this field is being directed towards the synthesis of PPP derivatives and related aromatic polymers with functional groups attached to, or incorporated in, the backbone. DuPont researchers, Kim and Webster,⁴⁹ were the first to synthesize a trifunctional benzene-based monomer (Figure 1-20). Self-condensation of 3,5-dibromobenzenboronic acid resulted in the synthesis of a hyperbranched macromolecule that is water soluble. It is interesting that the hyperbranched polymer resembles models of unimolecular micelles.

Not only carbonyl and ether functional groups, but also carboxylic acids and imides are compatible with the coupling conditions. Among them, ether functions may be a compatible site for the coupling reaction at the Pd-metal center. Syntheses to produce structurally perfect polymers were successful.⁵

Wallow and Novak⁵⁰ reported a new method of synthesizing a water soluble, rigid rod PPP derivative using a water soluble Pd(0) catalyst. The PPP

derivative with two carboxylic acid groups per quaterphenylene has all *para* linkages along its backbone (Figure 1-21). This work may be important for environmental considerations which require an avoidance of organic solvent.

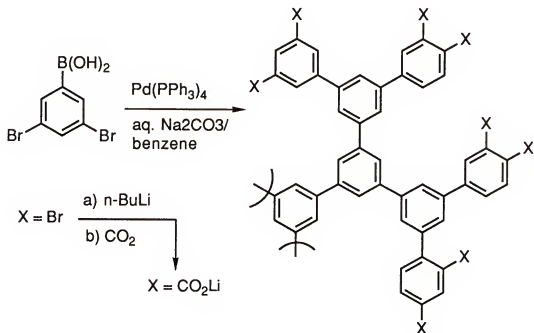


Figure 1-20 Structure of hyperbranched polyarylene synthesized using trifunctional monomer.

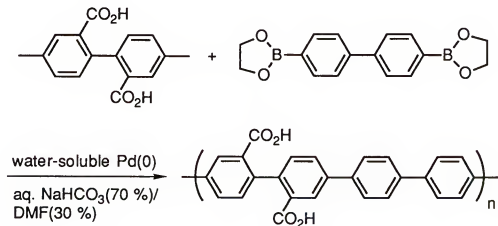
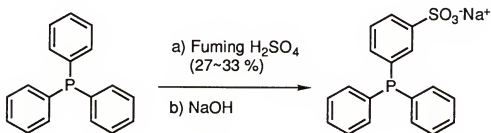


Figure 1-21 Scheme of water-soluble PPP synthesis using water-soluble Pd(0) catalyst.

1-9 Water-soluble Pd(0) Catalyst System

The Pd-catalyst generally used for Suzuki coupling is tetrakis(triphenylphosphine)palladium (0) in a heterogeneous system. Mixtures of aqueous base containing 0.2-2.0 mol% of NaHCO_3 or Na_2CO_3 with organic solvents such as toluene or benzene are used as the reaction medium with high temperatures showing better yields for coupling. This causes high boiling point solvents to be especially useful. Polar solvents such as THF or DMSO were also employed towards homogeneous reactions. But, Pd-catalyst or salt does not dissolve well in these solvents resulting in heterogeneous reaction.

(a) Monosulfonation [$\text{PPh}_2(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})$]



(b) Coulson's method

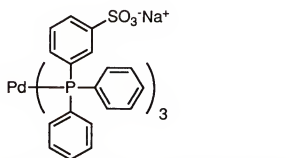


Figure 1-22 Scheme of water-soluble Pd(0) catalyst synthesis.

The water soluble Pd-catalyst used for the synthesis of Novak's water soluble polymer was first prepared by Casalnuovo and Calabrese.⁵¹ Wallow and Novak synthesized the water soluble Pd(0) catalyst modifying the method in the literature developed by Coulson.⁵² (Figure 1-22) This water soluble Pd-catalyst is very air-sensitive and somewhat light-sensitive.

For the synthesis of water-soluble PPP, Novak⁵¹ synthesized two different monomers for an A-A and B-B type polymerization. The ethylene glycol diester of 4,4'-biphenylenebis(boronic acid) served as a water-soluble monomer precursor that hydrolyzes rapidly in basic solution and thus is converted to a slightly water-soluble diboronic acid. The reaction mechanism of Pd-catalyzed coupling is explained as an oxidative insertion followed by reductive elimination which repeats throughout the catalytic coupling cycle⁵³ (Figure 1-23). Zero-valent Pd is inserted between both the aryl group and the Br and then oxidized. This complex goes on to react with arylboronic acid and produces a diaryl-substituted Pd-complex with four ligands. Finally, the Pd-complex with two ligands is eliminated leaving coupled diaryl product.

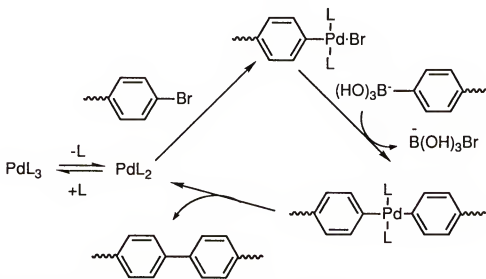


Figure 1-23 The catalytic coupling cycle using Pd-catalyst.

1-10 The Ambiguity of Endgroups and Rigidity of PPPs

The termination of the Yamamoto coupling method of polymerization is insufficiently understood. Trace amounts of water are believed to significantly contribute to the termination, reducing the activity of endgroups. An HPLC study of the low DP fractions showed three different peaks, indicating that there are three different endgroup combinations, H/H, H/Br, and Br/Br.⁴⁵ On the other hand, the Suzuki coupling method does not clearly show what types of end groups exist. Specific trimer or pentamer syntheses, coupling a substituted benzenediboric acid with either 1,4-dibromobenzene or 4,4'-dibromobiphenyl, using Pd-catalysis indicates that the Pd-catalyst does not affect remaining Br groups after the coupling reaction⁵⁴ (Figure 1-24).

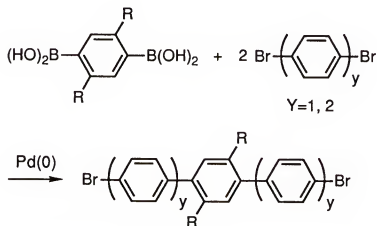


Figure 1-24 Trimer or pentamer synthesis using Pd-catalyst.

The proposed mechanism of Suzuki coupling involves the formation of a transient PdL_2 complex and its arylhalide adduct. (Refer to Figure 1-23.) Wallow and Novak^{53,55} explained the complexity of these adducts and suggested that the resulting adducts lead not only to desired product but also to exchanged products (Figure 1-25 (a)). Released triphenylphosphine from water-soluble Pd-catalyst forms tetraarylphosphonium ions. This reaction affects the endcapping of polymer chains with Br endgroups (Figure 1-25 (b)) and does

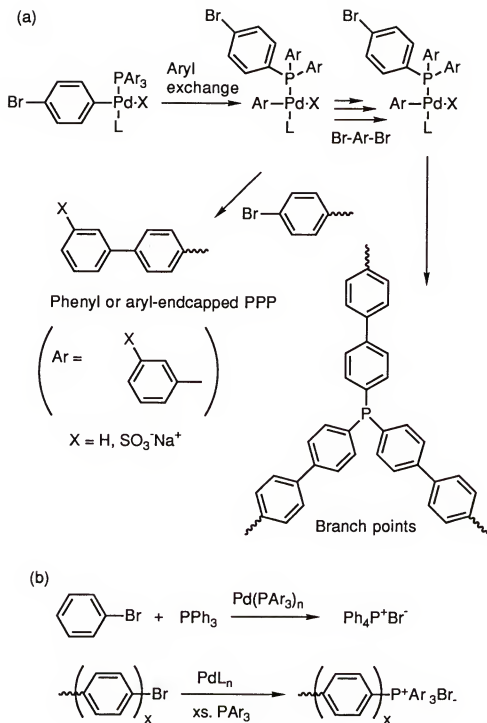


Figure 1-25 The proposed mechanism of (a) aryl exchange and (b) phosphonium ion formation.

not provide any information about exact endgroups. Novak⁵⁵ have suggested that triarylphosphonium sites exist in the polymers, eliminating their rigid-rod character. Thus, the use of Pd-catalyst without triphenylphosphine is being investigated for coupling.

1-11 Electronic and Optical Properties of PPP and Its Derivatives

Neutral PPP is an insulator which, once redox-doped, attains a fairly high conductivity (~ 500 S/cm).⁵⁶ Vapor phase doping of neutral PPP is carried out using AsF_5 or I_2 as oxidants or K as reductant. During the process, the dopant is incorporated as a charge-balancing ion such as AsF_6^- or I_3^- or K^+ .

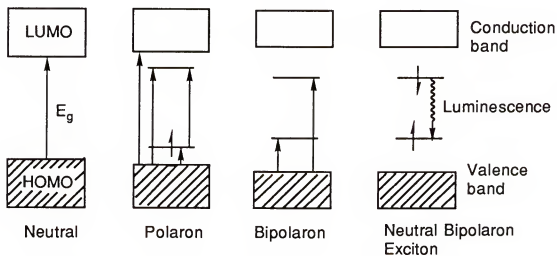


Figure 1-26 Band diagram of nondegenerated ground state conducting polymer.

The bandgap (E_g), defined as the energy difference between the valence band and the conduction band in a conjugated polymer, is determined using UV-Vis-NIR spectrophotometry. In the neutral form, a single electronic absorption occurs in the UV or visible region due to a transition between the HOMO and LUMO levels as shown in Figure 1-26. The figure shows a band diagram of a conjugated polymer with a nondegenerate ground state, and the possible transitions in the neutral, polaron, and bipolaron states. The band gap

of unsubstituted PPP is 3.0 eV.⁵⁷ A bipolaron creates a greater lattice distortion than a polaron and thus the gap is higher in the bipolaron model. The change in the optical absorption spectra of PPPs can be monitored using optoelectrochemical techniques.⁵⁸

Once PPP absorbs energy and excites electrons, it can emit at a lower energy and be luminescent. Most luminescence studies directed towards potential light emitting devices have been based on PPVs since their luminescence properties were reported.^{59,60} However, photoluminescence properties of PPPs have been more interesting since a blue-green light emission device based on PPP and poly(alkylfluorene) was recently introduced.^{61,62} Therefore, PPPs can be an important potential as a blue light emission material.

1-12 Motivation for the Synthesis of PPPs by the Introduction of Sulfonatopropoxy Substituents

Rigid chain polymers carrying bulky substituents can be soluble in common organic solvents as discussed in Section 1-7. Many of the PPP derivatives with alkyl substituents have been developed by Rehahn et al.^{48,54,63} However, the increased solubility comes at the expense of physical and electronic properties along with a larger torsional angle twist relative to unsubstituted PPP due to increased *ortho* hydrogen interactions as shown in Figure 1-27.⁶⁴ Further out of plane of consecutive aryl units result in a loss of the extended conjugation.

The introduction of sulfonatopropoxy groups onto PPP is described in this dissertation. The introduction of sulfonatopropoxy groups is expected to induce a greater water solubility without a significant loss of electronic properties. In addition, sulfonate groups are stable and improve water solubility independent of pH. Child and Reynolds⁶⁵ have proved that the

sulfonatopropoxy-substituted PPP derivative (PPP-OPSO₃) is a new type of water soluble, self-doped, and electroactive polyelectrolyte since the substituents impart an electronic stabilizing effect on positive charge carriers.

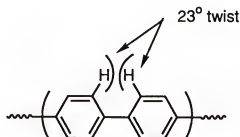


Figure 1-27 Structure of PPP with a 23° twist between two consecutive aryl units.

1-13 Synopsis of This Work

The work to be discussed in this dissertation is divided into two main sections. The first describes the synthesis and characterization of sulfo PBTs, and the second outlines the synthesis and characterization of water soluble PPPs with sulfonatopropoxy substituents. The overall theme of the dissertation is based on rigid-rod polyelectrolytes with aromatic backbones. The solution properties and viscosities will be emphasized with regard to the sulfonated PBTs, while water solubility and electronic properties will be of major focus with the sulfonatopropoxy substituted PPPs.

Part 1 of the work begins with the synthesis and purification of monomers for sulfo PBTs. PPA was synthesized mixing P₂O₅ with H₂PO₄ immediately before use. Optimum polymerization conditions were investigated by controlling the monomer concentration, monomer particle size, mixing techniques, reaction temperature, reaction time, P₂O₅ content, and polymer concentration. Intrinsic viscosities of the synthesized polymers were determined in MSA solutions at room temperature. Solubility tests of sulfo PBTs

were performed with a variety of organic solvents and acids. Mixed solvent systems were also explored resulting in best solubility.

Part 2 of the work describes the synthesis and characterization of PPPs with sulfonatopropoxy substituents. In the monomer synthesis, monomer purification has been emphasized. The pH dependence of polymerization under basic conditions was investigated and indirectly monitored using UV-Vis spectrophotometry. The λ_{max} of the $\pi-\pi^*$ absorption for the PPP with sulfonatopropoxy substituents was monitored for different samples synthesized. Fluorescence spectroscopy of these polymers indicates that the emission occurs at 420 ± 10 nm causing these polymers to be blue emitters. $\text{Pd}(\text{OAc})_2$ ⁶⁶ as well as water soluble Pd(0) catalysts were used to compare their effect on the degree of polymerization and pH dependence. Degrees of polymerization and molecular weight were monitored by means of an endcapping method using *t*-butylphenyl group. This study showed that the λ_{max} of the $\pi-\pi^*$ absorption tends to be limited regardless of the degree of polymerization for PPP carrying sulfonatopropoxy substituents.

CHAPTER 2

AROMATIC RIGID-ROD POLYELECTROLYTES BASED ON SULFONATED POLYBENZOBISTHIAZOLES

2-1 Sulfonated Polybenzobisthiazoles

In this chapter, the syntheses and properties of polybenzobisthiazoles (PBTs) with sulfonate substituents directly attached to the benzene ring of their backbone are discussed. Aromatic polyelectrolytes based on PBIs and PBTs have been developed and utilized for the improvement of processability.^{9-12,14-17} However, these polymers typically have aliphatic or ion-containing pendant alkyl chains which enhance interactions with solvent and improve solubility.

Unlike these polymers, the sulfo PBTs (*p*-sulfo PBT, *m*-sulfo PBT, and *m*-disulfo PBT) prepared in this work have sulfo groups directly attached to main chain *p*-phenylene units. These sulfonates are hydrophilic functional groups and the introduction of them onto intractable PBT backbones is expected to induce solubility in common solvents, possibly in water. Other expected advantages are the higher thermal stability of the aryl sulfonates relative to alkyl pendants and the possibility of retaining lyotropicity in the rigid-rod PBTs. The incorporation of sulfo groups is thus an important target for the development of PBTs with improved solubility. The work detailed here in Chapter 2 includes monomer syntheses, model compound syntheses, polymer syntheses, characterization of the synthesized polymers, and study of some important physical properties such as intrinsic viscosity and solubility.

2-2 General Experimental

2-2-1 Material Handling and Purification

Diacid monomers, 2-sulfoterephthalic acid sodium salt, 5-sulfoisophthalic acid sodium salt, and 2,4-disulfoisophthalic acid potassium salt are hygroscopic. Among them, 2-sulfoterephthalic acid and 5-sulfoisophthalic acid were not of sufficient purity for polymerization as purchased. Aqueous concentrated HCl was used for recrystallization to obtain high purity monomers for polymerization. After vacuum drying, the diacid monomers were stored in a dessiccator.

Disulfonation of *m*-xylene using fuming sulfuric acid, followed by oxidation of the methyl groups of *m*-xylene using KMnO₄ were carried out to produce 2,4-disulfoisophthalic acid.^{67,68} This product was also recrystallized from concentrated aqueous HCl, dried in a vacuum oven, and stored in a dessiccator. 2-Sulfobenzoic acid and 3-sulfobenzoic acid were purchased and purified using the above method for model compound synthesis.

The crude product of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) was recrystallized from concentrated acetic acid.^{2,4} Purified DABDT was stored in a dessiccator after vacuum drying.

Polyphosphoric acid (PPA) was freshly prepared immediately before use. The P₂O₅ content was controlled by changing the ratio (w/w) of P₂O₅ in 85% phosphoric acid. PPA is utilized as a solvent medium for polycondensation reactions in order to adsorb water released from the reaction. Therefore, the use of anhydrous P₂O₅ is important for the synthesis of fresh PPA. P₂O₅ was stored in a drybox as received and transferred under inert atmosphere. The prepared PPA was kept under argon until used. During dehydrochlorination of DABDT, the monomer was mixed slowly with PPA using mechanical stirring and finally dissolved evenly into the PPA.

Dialysis membranes were used for the purification of polymer products. Sulfo PBT polymers contain many side products, such as PPA oligomers from the reaction medium, MSA, and possibly sulfo PBT oligomers. These side products are not easily removed by precipitation of the polymers in water and dialysis is an excellent way to remove the impurities. A membrane with a 3,500 g/mol cut-off range was chosen for this purpose. Each membrane tube contained about 250 ml of sulfo PBT solution. These tubes were transferred into a 2 L distilled water-containing bath and the water changed twice daily. Three days of dialysis resulted in a sufficiently pure product to achieve a satisfactory elemental analysis and utilize for complete characterization.

2-2-2 General Characterization Method Used for Intermediate Products, Monomers, and Polymers

Intermediates, monomers, and polymer products were characterized using FT-IR and NMR spectroscopy. FT-IR spectra for all products were obtained using a Bio-Rad/Digilab FTS-40A spectrophotometer. For intermediates and monomers, KBr pellet samples were prepared for IR spectroscopy. The diffuse reflectance method was used for the polymer samples as they were found to be hard to grind. Samples for IR spectroscopy were prepared as a 5% dispersion in KBr.

For DABDT synthesis, three products including DABDT were sequentially prepared and their ^1H -NMR and ^{13}C -NMR spectra were obtained using a Varian XL-200 spectrometer. The same spectrometer was also used to obtain NMR spectra of 2-sulfoterephthalic acid sodium salt, 5-sulfoisophthalic acid sodium salt, 2,4-disulfoisophthalic acid potassium salt, 2-sulfobenzoic acid sodium salt, and 3-sulfobenzoic acid sodium salt. CDCl_3 , $\text{DMSO}-d_6$, and D_2O were used as solvents for NMR spectrometry.

^{13}C -NMR spectra of sulfo PBTs were not easily obtained using a 200 MHz NMR spectrometer because of the low sensitivity due to the sulfo PBT's limited solubility in NMR solvents. A Bruker 300 MSL spectrometer was used for sulfo PBT studies and gave reasonable resolution of the carbon peaks. High temperatures (ca. 80°C) were required to increase the solubility of the samples. Long term acquisitions (ca. acquisition number >12,000) were necessary to obtain a minimum resolution for analysis. Solvents used to obtain the NMR spectra were DMSO- d_6 for *p*-sulfo PBT, D_2SO_4 , for *m*-sulfo PBT, and D_2O for *m*-disulfo PBT.

Elemental analyses were carried out by Atlantic Microlab, Inc., Atlanta. The sulfur content in polymer products was monitored through the analysis. However, the phosphorous content is not easily analyzed in the presence of metals such as sodium and potassium ions. This analysis was done by Robertson Microlit Laboratories, Inc. Madison, New Jersey. Both companies reported accurate analysis result for carbon, hydrogen, and nitrogen. However, the sulfur content obtained from Robertson Microlit Laboratories, Inc. was somewhat lower than that of Atlantic Microlab, Inc.

Intrinsic viscosities of samples of sulfo PBTs samples were measured in MSA under an inert atmosphere at 30 °C using a Schott Ubbelohde Automatic viscometer. MSA was freshly distilled before use. All solutions were filtered through a 5 μm filter. Each concentration efflux-time was measured a minimum of 5 times and averaged. Intrinsic viscosity was obtained by extrapolation to zero concentration.

Onset degradation temperatures for the polymers were measured using thermogravimetric analysis (TGA). TGAs for sulfo PBT samples were performed in a nitrogen atmosphere using a Perkin-Elmer Series 7 thermal analysis system. For analysis, 2 to 10 mg samples were used and were heated at a rate

of 10 °C/min. Sulfo PBTs contain water due to the hygroscopic sulfonates. To remove this water, all samples were dried *in situ* by holding the temperature at 100 °C for 10 minutes prior to analysis.

2-3 Monomer Syntheses

Two different types of monomers, dicarboxylic acids and DABDT were used for sulfo PBT synthesis. Three different phthalic acids, 2-sulfoterephthalic acid sodium salt, 5-sulfoisophthalic acid sodium salt, and 2,4-disulfoisophthalic acid potassium salt (Figure 2-1), were used for the syntheses of *p*-sulfo PBT, *m*-sulfo PBT, and *m*-disulfo PBT, respectively.

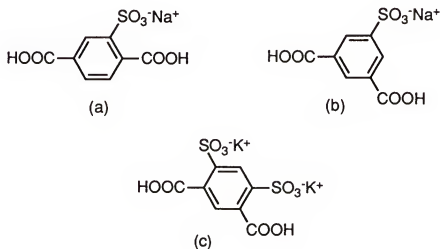


Figure 2-1 Structures of sulfonated monomers, (a) 2-sulfoterephthalic acid sodium salt, (b) 5-sulfoisophthalic acid sodium salt, and (c) 2,4-disulfoisophthalic acid potassium salt.

Among them, 2-sulfoterephthalic acid sodium salt (TCI America), 5-sulfoisophthalic acid sodium salt (Aldrich Chemical Co.) were commercially available, while 2,4-disulfoisophthalic acid potassium salt was synthesized. 2-Sulfobenzoic acid sodium salt and 3-sulfobenzoic acid sodium salt (Aldrich Chemical Co.) were used for the synthesis of model compounds before

polymerization. Terephthalic acid (TCI America) was also purchased and used as received in order to synthesize *p*-PBT as a standard polymer for the work.

2-3-1 Purification of Acid Monomers

The following procedure was employed for the purification of the acid monomers before use.

Into a 500 ml three neck round bottom flask equipped with water condenser were added 250 ml of aqueous concentrated hydrochloric acid and 5 g of acid monomer. The reaction medium was then heated and refluxed until the acid monomer dissolved completely. Slow addition of more acid monomer was carried out until dissolution was slow, giving a saturated solution. The solution was cooled at room temperature, filtered, and the crystals dried *in vacuo* at 80 °C.

2-3-2 Synthesis of 2,4-Disulfoisophthalic Acid Potassium Salt

Disulfonation of *m*-xylene was achieved using fuming sulfuric acid. The methyl groups of the *m*-xylene were subsequently oxidized to carboxylates using potassium permanganate. Acidification of the carboxylates, using 1 mol of aq. HCl, was followed by recrystallization from water. The following is a detailed procedure for the synthesis of 2,4-disulfoisophthalic acid potassium salt.

Into a 500 ml round bottom flask filled with 10.6 g of *m*-xylene (0.1 mol) was added 34.2 g of fuming sulfuric acid (SO₃ 20%, 0.3 mol) dropwise. The reaction was heated at 90 °C for 12 hours, then cooled in an ice-water bath. Solid crystals were collected by filtration. The product was neutralized in 100 ml of water solution using 1N potassium hydroxide. The solution volume was reduced by evaporation of water. Potassium *m*-xylene disulfonate was recrystallized from water at 0 °C and then dried *in vacuo* at 80 °C. A mixture of

14.4 g of potassium *m*-xylene disulfonate (0.031 mol), 50 g of potassium permanganate (0.31 mol), and 250 ml of water was heated at 90 °C for 10 hours with stirring. After reaction, a small amount of methanol was added to the reaction mixture to decompose the excess potassium permanganate. The manganese dioxide formed was filtered out. The filtrate was neutralized with aqueous concentrated hydrochloric acid and the water removed. The crude product was recrystallized from aqueous concentrated hydrochloric acid to give the final product, 2,4-disulfoisophthalic acid potassium salt.⁸ ¹³C-NMR (D₂O): δ 126.5, 127.3, 134.7, 143.1, 181.3.

2-3-3 Synthesis of 2,5-Diamino-1,4-benzenedithiol

2,5-Diamino-1,4-benzenedithiol dihydrochloride (DABDT), was prepared and purified using the method reported by Wolfe et al.⁴ The synthetic scheme shown in Figure 2-2 indicates that this reaction consists of thiourea formation, bromination, cyclization, ring cleavage, and acidification. 1,4-Phenylenediamine was reacted with ammonium thiocyanate to form 1,4-phenylenebis(thiourea) (**1**). The 1,4-phenylenebis(thiourea) was brominated and then heated to give cyclized product, 2,6-diaminobenzo[1,2-*d*:4,5-*d'*]bisthiol (**2**). The 2,5-dibromination condition is required for the ring closure as two different brominated products, 2,5-dibromo-1,4-phenylenebis(thiourea), and 2,3-dibromo-1,4-phenylenebis(thiourea), were possible in this reaction (Figure 2-3).

A small technical improvement was achieved in this reaction by careful control of reaction temperature for the bromination. Keeping the reaction temperature at 0 °C, with a slow addition of bromine, produced the desired product, prevented the formation of 2,3-dibromo-1,4-phenylenebis(thiourea).

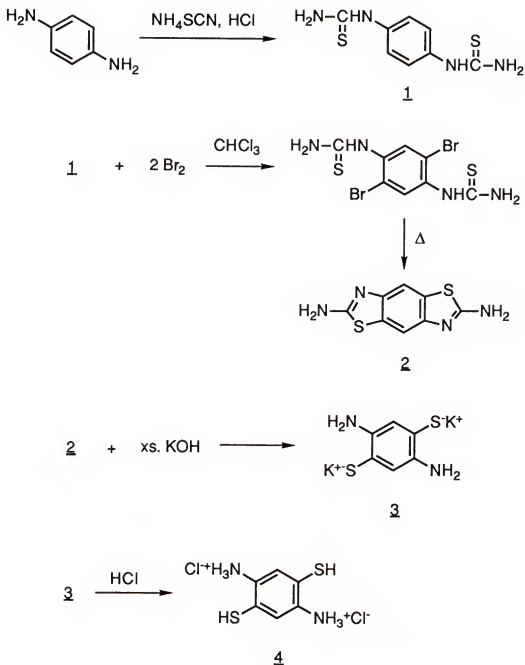


Figure 2-2 Synthetic scheme for 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT).

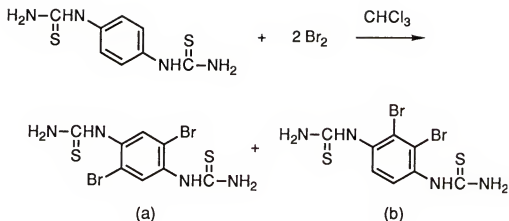


Figure 2-3 Structure of (a) 2,5-dibromo-1,4-phenylenebis(thiourea) and (b) 2,3-dibromo-1,4-phenylenebis(thiourea) resulting from the dibromination of 1,4-phenylenebis(thiourea).

The ring cleavage step was carried out under inert atmosphere to give 2,5-diamino-1,4-benzenedithiol potassium salt (**3**). The potassium salt product was found to be extremely air-sensitive, turning black-brown in air. After acidification by hydrochloric acid, stable final product, 2,5-diamino-1,4-benzenedithiol hydrochloride (DABDT) (**4**) was obtained. The detailed experimental procedure given below is divided into three steps as follows.

Synthesis of 1,4-phenylenebis(thiourea) (1)

Into a 500 ml round bottom flask were added 21.5 g of 1,4-phenylenediamine (0.2 mol) and 200 ml of deaerated water. Subsequently, 37.5 ml of aqueous concentrated hydrochloric acid and 5 g of charcoal were added. The mixture was warmed to 50 °C and transferred into another 500 ml flask equipped with water condenser. Ammonium thiocyanate (30 g, 0.8 mol) was added and the mixture was stirred at 90 °C for 24 hours. The light yellow, granular product precipitated out and collected by filtration. The product was washed with hot water and then dried *in vacuo* at 80 °C. ¹H-NMR (DMSO-*d*₆):

δ 4.6 (broad, 4H), 7.3 (m, 4H), 9.8 (m, 1H). ^{13}C -NMR (DMSO- d_6): δ 123.8, 135.4, 180.9.

Synthesis of 2,6-diaminobenzo[1,2- d :4,5- d']bisthiazole (2)

To a stirred suspension of 19.5 g of 1,4-phenylenebis(thiourea) (0.086 mol) in 200 ml of dry chloroform was added a 49 g of bromine (0.3 mol) in 100 ml of chloroform dropwise in ice-water bath. The orange-colored slurry was stirred at room temperature overnight and then heated at reflux for 24 hours. The mixture was cooled at room temperature. The orange solid was collected by filtration, washed with chloroform, and dried in the air. The dried solid was stirred with 200 ml of aqueous sodium bisulfide solution (5 %w/w). The crude product was recrystallized from 2 L of glacial acetic acid and dried at 80 °C. for 24 hours. ^1H -NMR (DMSO- d_6): δ 7.8. ^{13}C -NMR (DMSO- d_6): δ 109.5, 128.9, 147.1, 165.3.

Synthesis of 2,5-diamino-1,4-benzenedithiol hydrochloride (DABDT) (4)

Into a 500 ml flask were added 60.7 g of potassium hydroxide (0.93 mol) and 10 ml of deaerated water. The solution was allowed to cool at room temperature and then 15.0 g of 2,6-diaminobenzo[1,2- d :4,5- d']bisthiazole was added while the flask was swept with a stream of argon. The mixture was heated to the reflux temperature under argon purge for 5 hours and then cooled to room temperature. The volume of the resultant solution was reduced by transferring excess solution into another flask via canula. Yellow needles of the potassium salt (**3**) were dissolved in a 150 ml mixture of hydrochloric acid with water (20/80 v/v). A fine off-white powder of 2,6-diaminobenzo[1,2- d :4,5- d']bisthiazole formed rapidly. The monomer was recrystallized from 2 L of glacial acetic acid, collected by filtration, and then dried *in vacuo* at 90 °C for 24 hours. ^1H -NMR (DMSO- d_6): all broad peaks δ 6.93 , 7.44. ^{13}C -NMR (DMSO- d_6): δ 125.80, 128.44, 130.86.

2-4 Synthesis of Polyphosphoric Acid (PPA)

The key to successful polycondensation in solution for the synthesis of PBTs is the choice of solvent. PPA is used as solvent, catalyst, and dehydrating agent. PPAs are a continuous series of mixtures of condensed phosphoric acid oligomers with more than 14 repeat units² (Figure 2-4). The average value of n depends on the ratio of water to phosphorous pentoxide (P_2O_5). The various compositions of PPA are determined by the phosphoric acid (H_3PO_4) to P_2O_5 content. The H_3PO_4 (or P_2O_5) content of the mixture is defined as the weight of the H_3PO_4 (or P_2O_5) in the PPA divided by the total weight of the PPA. The P_2O_5 content is typically used to describe the reaction medium, because of its practical use in the PPA composition during polymerization. The viscosity of PPA depends on P_2O_5 content.

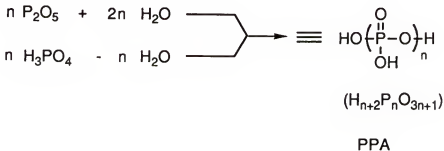


Figure 2-4 Structure of polyphosphoric acid (PPA) and its theoretical description according to P_2O_5 or H_3PO_4 content.

PPAs with 84.9 % P_2O_5 content were prepared by adding P_2O_5 to 85 % phosphoric acid.² The results shown in the literature indicate that the highest molecular weight of unsubstituted PBT are obtained when the P_2O_5 content is greater than 83 % during the entire reaction. The results also showed that the reaction mixture at the end of polymerization contained a P_2O_5 content greater

than 83 % at low polymer concentrations (<6 %) when the P₂O₅ content during dehydrochlorination is higher than 85 %.

The use of lower P₂O₅ content (e.g. 78 %) gives an advantage to mixing of the monomers due to a low viscosity of the 78 % P₂O₅ relative to the 85 % P₂O₅. On the other hand, a higher P₂O₅ content over 83 % is required in order to obtain high molecular weight. The addition of P₂O₅ at the beginning of polymerization is typically carried out to increase the P₂O₅ content to over 83 % at the end of polymerization. However, this method was not employed in this work due to a stirring problem with the additional P₂O₅. The following procedure was used for the syntheses of the PPAs with P₂O₅ content of 85 %.

Synthesis of PPA with P₂O₅ contents of 85 %

Into a 250 ml three neck flask equipped with a mechanical stirrer were charged 26.2 g of P₂O₅ and 17.2 g of 85 % H₃PO₄ (1.52/1 w/w) under argon purge. The heterogeneous mixture was heated at 150 °C and stirred slowly for 6 hours until P₂O₅ dissolved completely in H₃PO₄, yielding a solution containing 85 % P₂O₅. The product was cooled to room temperature and then stored under argon prior to use.

2-5 Syntheses of Two Model Compounds

2-5-1 Syntheses of Model Compounds

Two compounds were synthesized as structural models to evaluate the benzothiazole ring formation of the sulfonated PBT repeat units⁶⁹ (Figure 2-5). The model compound syntheses indicated that the *ortho* and *meta* sulfonate groups of the acid monomers do not affect the formation of the thiazole linkage.

The same synthetic conditions, used for the synthesis of *p*-PBT in the literature, were employed for the syntheses of the model compounds. The detailed synthetic procedure is described as follows.^{2,4}

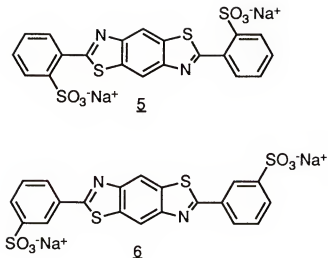


Figure 2-5 Structures of model compounds, bis(2-sulfophenyl)benzo [1,2-*d*:4,5-*d'*]bisthiazole sodium salt (**5**), and bis(3-sulfophenyl)benzo [1,2-*d*:4,5-*d'*]bisthiazole sodium salt (**6**).

Synthesis of bis(2-sulfophenyl)benzo[1,2-*d*:4,5-*d'*]bisthiazole sodium salt (**5**)

To a 250 ml three neck flask, fitted with mechanical stirrer and containing 48.5 g of freshly prepared PPA (84.9 % P_2O_5), was added 1.961 g of DABDT (8.000 mmol) . The contents were stirred at room temperature for 24 hours, then heated to 70 °C for 36 hours until the dehydrochlorination was complete at which time 3.586 g (16.000 mmol) of 2-sulfobenzoic acid sodium salt was added. The reaction mixture was heated sequentially.: 110 °C for 6 hours, 165 °C for 12 hours, 180 °C for 12 hours, and 195 °C for 12 hours. The dark solution was poured into cold CH_3OH and cooled until a white precipitate formed. The product was washed with cold CH_3OH and dilute NH_4OH , dried in air, and recrystallized from toluene yielding 2.91 g (66.4 %). ^{13}C -NMR ($DMSO-d_6$) of **5**: δ = 168.9 (C4), 150.1 (C5), 146.2 (C6), 135.7 (C2), 131.5 (C3), 129.6, 128.9, 127.5, 115.9, and 114.7 (C1, C7, C8, C9, and C10).

Synthesis of bis(3-sulfophenyl)benzo[1,2-*d*:4,5-*d'*]bisthiazole sodium salt (6)

Into a 250 ml three neck flask, fitted with mechanical stirrer and containing 48.5 g of freshly prepared PPA (84.9 % P₂O₅), was added 1.961 g of DABDT (8.000 mmol). The contents were stirred at room temperature for 24 hours, then heated to 70 °C for 36 hours until the dehydrochlorination was complete, at which time 3.586 g (16.000 mmol) of 3-sulfobenzoic acid sodium salt was added. The reaction mixture was heated sequentially: 110 °C for 6 hours, 165 °C for 12 hours, 180 °C for 12 hours, and 195 °C for 12 hours. The dark solution was poured into cold CH₃OH and cooled until a white precipitate formed. The product was washed with cold CH₃OH and dilute NH₄OH, dried in air, and recrystallized from toluene yielding 2.73 g (62.3 %) ¹³C-NMR (DMSO-*d*₆) of **6**: δ = 168.3 (C4), 151.9 (C5), 149.1 (C7), 134.4 (C2), 132.7 (C3), 129.7, 129.0, 128.1, 124.5, and 116.4 (C1, C6, C8, C9, and C10). ANAL. Calcd. for C₂₀H₁₀N₂S₄O₆Na₂•2.2 H₂O: C, 38.70; H, 2.22; N, 4.51; S, 20.66; Na, 7.41. Found: C, 37.88; H, 2.58; N, 4.34; S, 20.12; Na, 7.13.

2-5-2 Characterization of Model Compounds

The formation of the thiazole linkage was characterized using ¹³C-NMR spectroscopy. As seen Figure 2-6, the presence of strong peaks at 168.9 and 168.3 ppm in the ¹³C-NMR spectra of bis(2-sulfophenyl)benzo[1,2-*d*:4,5-*d'*]bisthiazole sodium salt (**5**) and bis(3-sulfophenyl)benzo[1,2-*d*:4,5-*d'*]bisthiazole sodium salt (**6**) respectively, indicates the formation of the thiazole linkage. These results are further supported by the absence of carboxylate peaks at 175.4 and 171.8 ppm observed for 2-sulfobenzoic acid sodium salt and 3-sulfobenzoic acid sodium salt, respectively.

While the assignments made for each specific carbon are somewhat tentative, it is important to note that each molecule displays the proper numbers

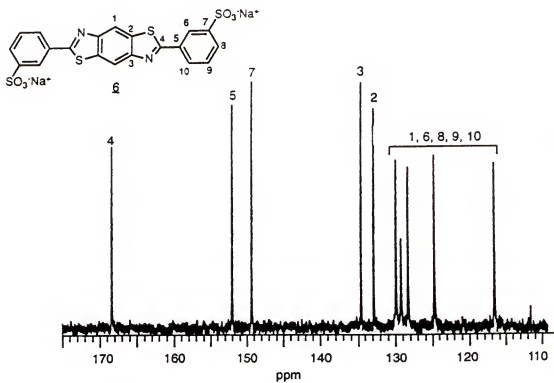
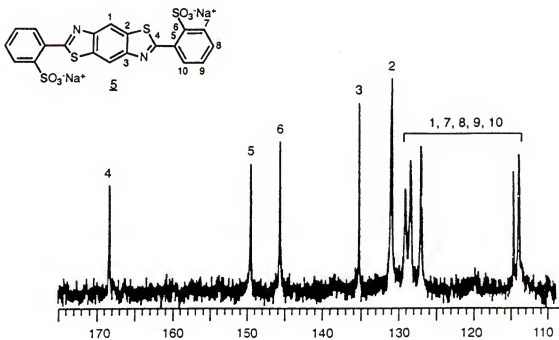


Figure 2-6 ^{13}C -NMR spectra of model compounds, 5, and 6.

of resonances. The structure of the sulfo PBTs will contain linkages illustrated by these model compounds.

The FT-IR spectra of the model compounds proved the existence of two strong absorption bands indicating asymmetric and symmetric S=O stretching vibrations sulfonate groups found at 1250-1190 and 1100-1030 cm^{-1} (Figure 2-7).

2-6 Polymer Syntheses

All polymerizations, as illustrated in Figure 2-8, were run using the reaction conditions outlined in the experimental section for the model compound syntheses.

2-6-1 *p*-Sulfo PBT

p-Sulfo PBT was synthesized using the modified Wolfe procedure.⁴ The main purpose of sulfo PBT synthesis is to obtain a *p*-PBT with enhanced solubility. One critical condition to obtaining high molecular weight is that the polymerization should be conducted in the nematic phase. For this purpose, three different polymer concentrations, 3.9, 5.6, and 11.2 wt % were employed. Among those values, 5.6 wt % polymer was interesting since the polymer concentration value resulted in *p*-PBT with highest intrinsic viscosity.

The P₂O₅ content near the end of polymerization was maintained between 82 % and 84 % during the polymerization for the production of high molecular weight . During the dehydrochlorination, DABDT was mixed with PPA. DABDT powders were ground in a mortar before use in order to increase surface area for better contact with PPA. 2-Sulfophthalic acid sodium salt was also ground in the mortar before use to obtain an increased surface area. As soon as the 2-sulfophthalic acid sodium salt was added, the mixture turned yellow to green. Through stepwise increase of reaction temperature, the

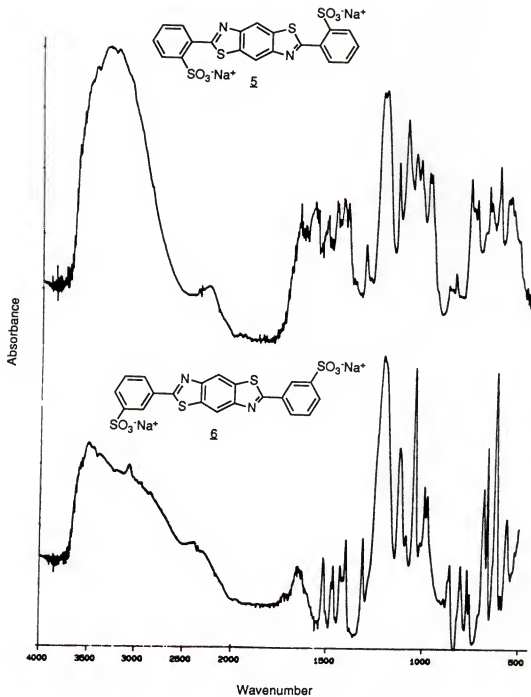


Figure 2-7 FT-IR spectra of model compounds, 5, and 6.

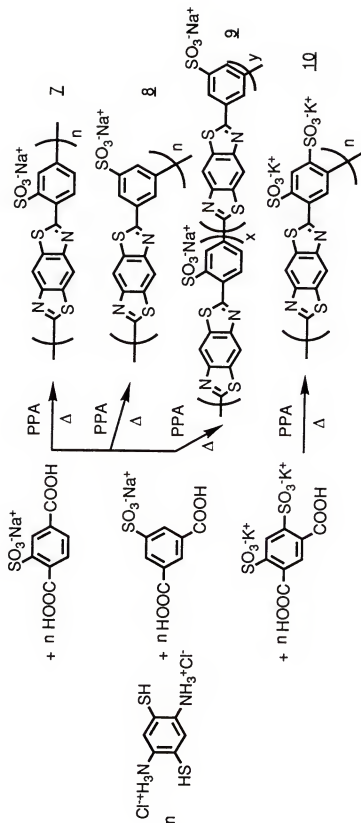


Figure 2-8 Synthetic routes for *p*-sulfo PBT, *m*-sulfo PBT, and *m*-disulfo PBT

mixture turned black. The mixture was dissolved in MSA and subsequently poured into water to precipitate the sulfo PBT as a dark brown solid. The *p*-sulfo PBT was purified by dialysis for a week to remove excess monomers, oligomers, and acids. It swelled considerably upon exposure to water. Upon dialysis, it turned violet/black.

Synthesis of *p*-sulfo PBT (7)

Into a 250 ml three neck flask, equipped with mechanical stirrer were placed 48.5 g of freshly prepared PPA for a resulting polymer concentration of 5.6 % (13.7 g for a polymer concentration of 11.6 %) and 1.961 g (8.000 mmol) of DABDT. The mixture was stirred under argon atmosphere at room temperature for 24 hours, then heated to 70 °C for 36 hours until the dehydrochlorination was complete. Into the solution 2.145 g (8.000 mmol) of 2-sulfoterephthalic acid sodium salt was added and mixed by rapid stirring at 110 °C. For the polymer concentration of 11.6 %, 8.2 g of P₂O₅ was added to adjust the polymer concentration after dehydrochlorination. The reaction mixture was then heated as follows: 110 °C for 6 hours, 165 °C for 12 hours, 180 °C for 12 hours, and 195 °C for 12 hours. MSA (200 ml) was added to the final reaction medium to dissolve the slurry. The solution was poured into 4 L of deionized water to yield a dark brown swollen product. The product was collected by filtration and washed with water. The polymer was dialyzed in distilled water for 5 days using a membrane with a molecular weight cut off range of 3500 g/mol and dried *in vacuo* at 120 °C for 12 hours yielding 2.60 g (88.3 %). ¹³C-NMR(DMSO-*d*₆): δ= 168.8 (C4), 154.5 (C5), 150.2 (C8), 146.2 (C6), 135.7 (C3), 131.5 (C2), 129.6, 128.9, 127.5, and 117.1 (C1, C7, C9, and C10). ANAL. Calcd. for [C₁₄H₅N₂S₃O₃Na•2.5 H₂O]_x: C, 40.68; H, 2.42; N, 6.78; S, 23.27; Na, 5.56. Found: C, 40.69; H, 2.46; N, 6.73; S, 23.19; Na, 5.63.

2-6-2 *m*-Sulfo PBT

m-Sulfo PBT was synthesized in order to compare its rigidity with *p*-sulfo PBT's. The same synthetic conditions for *p*-sulfo PBT were used for *m*-sulfo PBT. The polycondensation reaction was run in freshly prepared PPA at polymer concentrations of 3.9 and 5.6 %.

The P₂O₅ content near the end of polymerization was maintained between 82 % and 84 % for the production of high molecular weight. 5-Sulfoisophthalic acid was also ground in a mortar before use to obtain an increased reaction surface area. As soon as the 5-sulfoisophthalic acid was added, the mixture turned yellow to green. Through stepwise increase of reaction temperature, the mixture turned dark green. The mixture dissolved in MSA and was subsequently poured into water to precipitate the *m*-sulfo PBT as a dark brown-green solid. The *m*-sulfo PBT was purified by dialysis for a week to remove excess monomers, oligomers, and acids. It swelled considerably upon exposure to water. It turned pale violet after drying, decreasing its volume significantly.

Synthesis of *m*-sulfo PBT (8)

Into a 250 ml three neck flask fitted with a mechanical stirrer were placed 48.5 g of freshly prepared PPA and 1.961 g (8.000 mmol) of DABDT. After the dehydrochlorination was complete, 2.145 g (8.000 mmol) of 5-sulfoisophthalic acid sodium salt was added. The polymerization was performed as described above. The recovered polymer, *m*-sulfo PBT was dried *in vacuo* at 120 °C for 12 hours yielding 2.56 g (86.9 %). ANAL. Calcd. for [C₁₄H₅N₂S₃O₃Na]: C, 45.05; H, 1.37%; N, 7.60; S, 26.11; Na, 6.24. Found: C, 44.44; H, 2.73; N, 7.36; S, 16.89; Na, 0.33; P, <0.03.

2-6-3 Copolymers

Copolymers 9a, 9b, and 9c with *p*-sulfo PBT and *m*-sulfo PBT repeat units were synthesized using the procedures detailed above. The ratio of monomers (2-sulfoterephthalic acid/5-sulfoisophthalic acid) was 75/25 (9a), 50/50 (9b), and 25/75 (9c) respectively.

2-6-4 *m*-Disulfo PBT

m-Disulfo PBT was synthesized in the same manner described above. The disulfonated PBT structure is unique as it contains *meta* linkages as well as two sulfonates per repeat unit. This offers a good comparison to the structure of the monosulfo PBTs, and their copolymers, because of its water-solubility. The polycondensation reaction was run in freshly prepared PPA at a polymer concentration of 3.9 %.

The P₂O₅ content near the end of polymerization was maintained over 83 % during the polymerization for the production of high molecular weight. 2,4-Disulfoisophthalic acid was also ground in mortar before use to obtain an increased surface area. As soon as the 2,4-disulfoisophthalic acid was added, the mixture turned yellow to green. Through stepwise increase of reaction temperature, the mixture turned dark brown. The mixture was dissolved in water. The *m*-disulfo PBT solution was purified by dialysis for a week to remove excess monomers, oligomers, and acids. It swelled considerably upon exposure to water. It turned brownish violet after drying as a brittle solid.

Synthesis of *m*-disulfo PBT (10)

Into a 250 ml flask equipped with mechanical stirrer were charged 50 g of freshly prepared PPA and 1.838 g (7.500 mmol) DABDT. The reaction mixture was stirred at room temperature for 24 hours and then heated at 70 °C. The reaction was allowed to progress at 70 °C for 48 hours and heated to 110 °C

for 1 hour after which 3.026 g (7.500 mmol) of 2,4-disulfoisophthalic acid was added. The reaction mixture was then heated as follows: 110 °C for 6 hours, 165 °C for 18 hours, 180 °C for 12 hours, and 195 °C for 12 hours. A 50 ml aliquot of water was poured into the flask. The reaction medium was precipitated into acetone producing a light brown precipitate. The product was washed with acetone and dialyzed in deionized water for 7 days using a membrane with molecular weight cut off range of 3500 g/mol . The polymer obtained was dried *in vacuo* at 120 °C for 12 hours yielding 2.45 g (74.6 %). ^{13}C -NMR (D_2O): δ = 167.0 (C4), 149.8 (C5), 143.7 (C6), 135.6 (C3), 133.2 (C2), 128.1, 127.4, 115.5 (C1, C7, C8). ANAL. Calcd. for $[\text{C}_{14}\text{H}_4\text{N}_2\text{S}_4\text{O}_6\text{K}_2 \cdot 2.5 \text{H}_2\text{O}]_x$: C, 33.46%; H, 0.80%; N, 5.58%; S, 25.50%; K, 15.54%. Found: C, 33.02%; H, 3.07%; N, 5.66%; S, 24.94%; K, 6.11%.

2-7 Structural Characterization of Sulfo PBTs

The molecular level structure of the sulfo PBTs was characterized by ^{13}C -NMR, FT-IR, and elemental analysis. ^{13}C -NMR spectra were run at elevated temperature (80 °C) due to the high viscosity of the polymer solutions in $\text{DMSO}-d_6$, D_2SO_4 , and D_2O . Figure 2-9 shows the ^{13}C -NMR spectra for *p*-sulfo PBT and *m*-disulfo PBT.

All of the observed peaks are broad, even after long term acquisitions. However, peak assignment was carried out based on comparison with model compound spectra. The peak at 165-168 ppm (peak 4) indicates the successful formation of the thiazole carbon and the peak at 150-153 ppm (peak 5) is due to the carbon attached to the thiazole ring on the sulfonated phenylene ring. The peak of the sulfonated aromatic carbon is found at 143-149 ppm. (peak 6) Four unsubstituted aromatic carbons are shown within the range of 115-138 ppm.

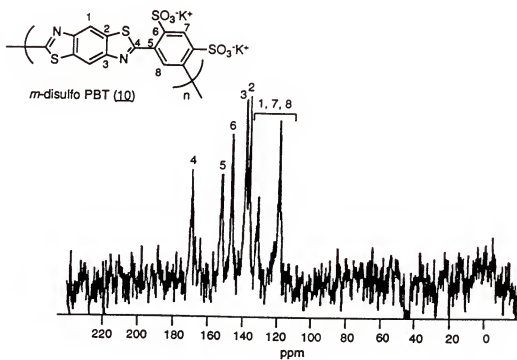
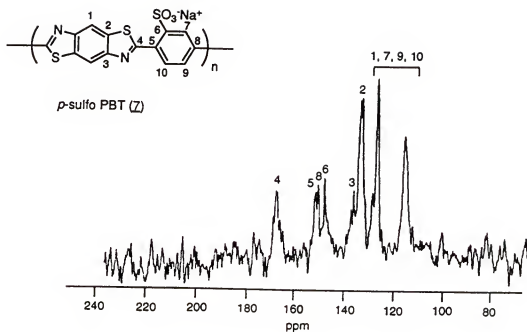


Figure 2-9 ¹³C-NMR spectra of *p*-sulfo PBT and *m*-disulfo PBT.

These results are consistent with the peak assignments made earlier for the model compounds bis(2-sulfophenyl)benzo[1,2-*d*:4,5-*d'*]bisthiazole and bis(3-sulfophenyl)benzo[1,2-*d*:4,5-*d'*]bisthiazole. Comparison of the ^{13}C -NMR spectra of *p*-sulfo PBT and the model compound, bis(2-sulfophenyl)benzo[1,2-*d*:4,5-*d'*]bisthiazole, shows a peak in the model compound at 116-117 ppm not present in the polymer, while a new peak appears at 151-153 ppm, indicating the formation of the *para* linkage between monomers after polymerization.

The ^{13}C -NMR spectrum of *m*-disulfo PBT shows 8 different carbon peaks due to a high degree of symmetry in the polymer repeat unit during polymerization, while *p*-sulfo PBT shows 10 different carbon peaks. The peak at 165-168 ppm (peak 4) indicating the thiazole carbon, the peak at 150-153 ppm (peak 5) due to the carbon attached to the thiazole-substituted carbon on the sulfonated phenylene ring, and the peak of the sulfonated aromatic carbon at 143-149 ppm (peak 6). In addition, three unsubstituted aromatic carbon peaks are shown within the range of 115-130 ppm.

Unfortunately, the ^{13}C -NMR spectra of *m*-sulfo PBT indicated a problem in determination of the structure of the *m*-sulfo PBT. As shown in Figure 2-10, the peak at 165-168 ppm indicating the thiazole rings have formed. However, the peak at 150-153 ppm due to the thiazole-substituted carbon of the sulfonated phenylene ring and the peak of the sulfonated aromatic carbon at 143-149 ppm are not present. In addition, a low sulfur content (17 % found compared to 26 % expected) was determined by elemental analysis for the *m*-sulfo PBT. Therefore, a combination of ^{13}C -NMR and elemental analysis results suggests that, during the synthesis of *m*-sulfo PBT, most of the sulfonate moieties were lost (Figure 2-10). However, it should be noted that no carbonyl carbon peaks were evident in the ^{13}C -NMR spectra of the *m*-sulfo PBT or any of the other polymers.

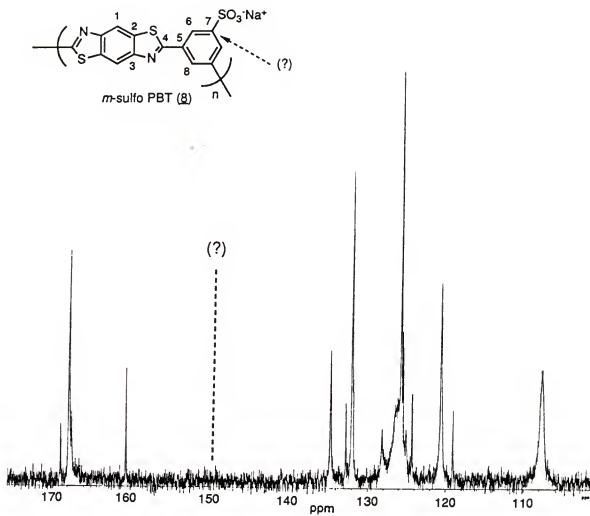


Figure 2-10 ^{13}C -NMR spectrum of *m*-sulfo PBT.

The FT-IR spectra of *p*-sulfo, *m*-sulfo, *m*-disulfo-PBTs were compared with an FT-IR spectrum of a *p*-PBT that was synthesized as a control (Figure 2-11). The presence of sulfonate groups on the sulfo PBTs are visible as two strong absorption bands which are due to asymmetric and symmetric S=O stretching vibrations at $1250\text{--}1190\text{ cm}^{-1}$ and $1100\text{--}1030\text{ cm}^{-1}$, respectively. The broad peak at $3400\text{--}3500\text{ cm}^{-1}$ indicates O-H stretching vibration due to water as the sulfo PBTs are highly hygroscopic.

Each spectrum also exhibits aromatic C-H stretching at $3050\text{--}3100\text{ cm}^{-1}$ and aromatic C=C ring stretching at $1590\text{--}1610\text{ cm}^{-1}$, $1510\text{--}1500\text{ cm}^{-1}$, and $1390\text{--}1410\text{ cm}^{-1}$. The weak peak at $1650\text{--}1680\text{ cm}^{-1}$ is due to C=O stretching and may be indicative of the end groups for each polymer chain. However, the peak at $1650\text{--}1680\text{ cm}^{-1}$ of *m*-sulfo PBT is relatively stronger than that of *p*-sulfo PBT, *m*-disulfo PBT, or *p*-PBT. This result suggests some incomplete ring closure.

Elemental analyses were reported for *p*-sulfo PBT and *m*-disulfo PBT in Section 2-6. The results are in good agreement with the calculated values of the proposed structures after adsorbed water content is considered. It should be noted that the elemental analysis results of *m*-disulfo PBT shows some loss of counteranions after a long period of dialysis. As noted above, the analysis of *m*-sulfo PBT is consistent with sulfonate loss.

2-8 Intrinsic Viscosity Measurements of Sulfo PBTs

The intrinsic viscosities of *p*-sulfo PBT, *m*-sulfo PBT and their copolymers were compared with standard non-sulfonated *p*-PBT (11a) prepared as a control and a *p*-PBT (11b) obtained from Wright-Patterson Air Force Base (WPAFB). The intrinsic viscosity measurements were carried out by D. Cameron in our group. The purpose of the comparison was to infer the relative

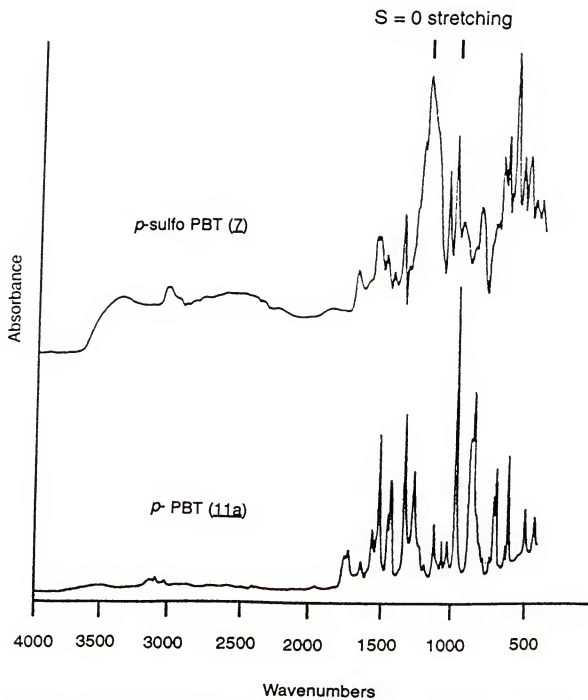


Figure 2-11 FT-IR spectra of *p*-sulfo, *m*-sulfo, and *m*-disulfo PBTs compared with non-sulfonated *p*-PBT.

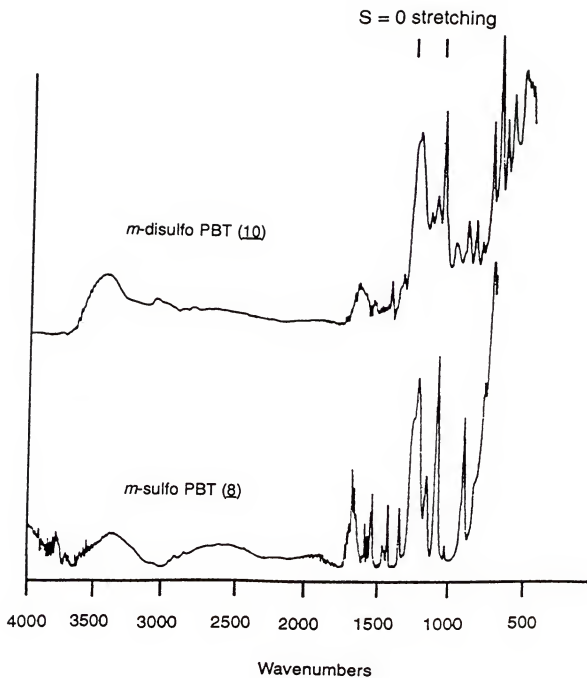


Figure 2-11 Continued

Table 2-1 Polymer concentrations and intrinsic viscosities for *p*-sulfo PBT, *m*-sulfo PBT, their copolymers, and *m*-disulfo PBT compared with *p*-PBT.

Polymer	ID	<i>para</i> %	Polymer conc. in PPA (w/w %)	Intrinsic viscosity (dL/g)
<i>p</i> -sulfo PBT	<u>7a</u>	100	3.9	0.84
<i>p</i> -sulfo PBT	<u>7b</u>	100	5.6	2.47
<i>p</i> -sulfo PBT	<u>7c</u>	100	5.6	3.00
<i>p</i> -sulfo PBT	<u>7d</u>	100	11.2	1.87
<i>m</i> -sulfo PBT	<u>8a</u>	0	3.9	0.19
<i>m</i> -sulfo PBT	<u>8b</u>	0	5.6	0.37
<i>p/m</i> -sulfo PBT	<u>9a</u>	75	3.9	0.74
<i>p/m</i> -sulfo PBT	<u>9b</u>	50	3.9	0.54
<i>p/m</i> -sulfo PBT	<u>9c</u>	25	3.9	0.37
<i>m</i> -disulfo PBT	<u>10</u>	0	3.9	0.29
<i>p</i> -PBT (control)	<u>11a</u>	100	5.6	1.80
<i>p</i> -PBT (WPAFB)	<u>11b</u>	100	-	14.0

molecular weights of the polymers synthesized and to make observations regarding the effects of *meta* linkages along the polymer backbone. The viscosity results according to different polymerization concentrations in MSA were summarized in Table 2-1.

Several attempts were made to produce high molecular weight all *p*-sulfo PBT. Polymer samples 7a-7d represent our efforts to produce optimum material. Intrinsic viscosities ranging from 14-30 dL/g have been reported,² and have been confirmed with WPAFB standard PBT. The intrinsic viscosities for the *p*-PBT synthesized as a control are lower than the WPAFB standard *p*-PBT.

Based on Mark-Houwink coefficients² published for *p*-PBT, a molecular weight of approximately 8,100 g/mol for the non-sulfonated *p*-PBT prepared as a control was achieved, versus 25,000 g/mol for the WPAFB-produced standard *p*-PBT.

The low intrinsic viscosity of our non-sulfonated *p*-PBT control suggest that electrostatic interactions of the ionic sulfonated monomers are not limiting the molecular weight of our sulfo PBTs. It is unlikely that the ionic nature of the substituted terephthalic acid contributed to the lower viscosities observed in the sulfo PBTs, as the control sample yielded intrinsic viscosities in the same range as the sulfonated polymers.

Applying the Mark-Houwink coefficients for PBT as representative of the approximate sulfo PBT coefficients, a molecular weight on the order of 10,000 g/mol has been achieved for *p*-sulfo PBT. The limiting factors in production of high molecular weight polymer appear to be the viscosity of the reaction medium and the control of stoichiometry. These limitations may result from the relatively small batch sizes used and the difficulties in maintaining a well-stirred reaction medium.

The incorporation of *meta* linkages into the polymer chain reduced the intrinsic viscosity, as evidenced by the behavior of the copolymers. Indeed, the decrease in viscosity scales directly with the decrease in *para* linkages, down to the 25% *para* polymer which behaves identically to the all *meta* linked polymer. The more flexible nature of these polymers suggests that they may be candidates for molecular composites with all *para* PBT.

Composites of rigid-rod and random coil polymers are of interest as they exhibit favorable physical properties. Tan and Arnold have made ionic molecular composites of *p*-PBT with the sulfo-containing NaPAMPS [2-poly(acryloamido-2-methylpropanesulfonic acid sodium salt)].⁷⁰ It is expected

the enthalpy of mixing of *p*-PBT with sulfo PBT will be more favorable, enhancing the stability of the composite formed.

Viscosity studies were also carried out in neutral DMSO. At low concentrations, an increase in the reduced viscosity of the all *p*-sulfo PBT samples was observed. This behavior was suppressed in DMSO solutions containing 0.01 M lithium chloride. This behavior is not expected to be indicative of the polyelectrolyte effect as the rigid chains are already fully extended. Difficulties in isolating the polymer with deprotonated imine moieties on the repeat unit render this anomalous solution behavior suspect. Aggregation phenomenon has been observed in rigid rod systems and the polyampholyte nature of the protonated imine polymer is expected to further contribute to this behavior.

2-9 Solubility Studies

One important goal in synthesizing these sulfonated polymers, including their copolymers, was to enhance solubility with sulfonate groups. A number of organic and aqueous medium were evaluated as solvents for these polymers, as shown in Table 2-2, where the neat polymers were exposed to solvents at room temperature. Solubility was inferred from the degree of dissolution of polymer in the dilute regime (5 % w/v), while the sulfo PBTs retained solubility in strong acids. It was interesting that the sulfo PBTs exhibit increased solubility in some polar aprotic solvents, most notably DMSO, while *p*-PBT standard was not soluble in DMSO at all. *m*-Sulfo PBT was expected to dissolve better in DMSO than *p*-sulfo PBT due to *meta* linkage. However, the opposite was found. Moreover, *m*-disulfo PBT dissolved better in DMSO than *m*-sulfo PBT. These results may support the assumption that the sulfo groups of *m*-sulfo PBT were lost during polymerization.

Table 3-3 Solubility test results for sulfo PBTs compared with non-sulfonated PBT.

Polymer	ID	para %	Solvent									
			DMSO	DMF	NMP	DMAC	MSA	H ₂ SO ₄	PhNO ₂	5%NaOH	Acetone	MSA/CH ₂ Cl ₂
<i>p</i> -sulfo PBT	<u>Za</u>	100	+	x	x	x	++	+++	x	x	x	+++
<i>p</i> -sulfo PBT	<u>Zb</u>	100	+	x	x	x	++	+++	x	x	x	+++
<i>m</i> -sulfo PBT	<u>8a</u>	0	o	x	o	o	+++	++	x	x	x	+++
<i>p</i> / <i>m</i> -sulfo PBT	<u>9a</u>	75	+	o	o	x	+++	++	x	x	x	+++
<i>p</i> / <i>m</i> -sulfo PBT	<u>9b</u>	50	+	o	+	x	+++	++	x	x	x	+++
<i>p</i> / <i>m</i> -sulfo PBT	<u>9c</u>	25	++	+	o	o	+++	+++	x	x	x	+++
<i>m</i> -disulfo PBT	<u>10</u>	0	+	x	x	x	+	++	x	++	x	+++
<i>p</i> -PBT	<u>11a</u>	100	x	x	x	x	+++	++	x	x	x	+++
<i>p</i> -PBT	<u>11b</u>	100	x	x	x	x	+++	+	x	x	x	+++

X = insoluble, o = very slightly soluble, + = slightly soluble, ++ = moderately soluble, and +++ = very soluble

Use of highly polar solvents such as DMF, NMP, DMAc, nitrobenzene, and acetone did not result in an improved solubility for *p*-sulfo PBT, *m*-sulfo PBT, and *m*-disulfo PBT. *m*-Disulfo PBT exhibited its highest solubility in water, and was moderately soluble in 5 % aqueous NaOH. The disulfonated polymer also dissolved in methanol, ethanol, and isopropanol, as well as in strong acids.

Solubility in organic solvents was increased by predissolving the polymers in MSA then exposing them to organic solvents resulting in mixtures containing approximately 3 % MSA. This approach was performed by D. Cameron in our group and the results revealed enhanced solubility in polar aprotic and chlorinated solvents.

A mixed solvent system of MSA and CH₂Cl₂ proved to be the most aggressive of the room temperature solvents examined. (Note: Mixing of strong acids and chlorinated solvents should be carried out cautiously as reactions may occur at elevated temperature, potentially yielding phosgene. In this work, no gas evolution was detected and these solutions were always maintained at room temperature.)

All of the polymers listed in Table 2-2 dissolved in 80/20 (w/w) MSA/CH₂Cl₂ readily at room temperature. Dissolution of *p*-PBT in pure MSA (less than 1 % w/w) was accomplished by heating overnight with stirring. The same polymer dissolved in 80/20 MSA/CH₂Cl₂ within one hour without heating. The *p*-PBT control (lower molecular weight) dissolved even more quickly. The sulfonated PBTs required longer times and the order of dissolution followed from the all *meta* linked polymer (shortest dissolution time) to the all *para* linked polymer (longest dissolution time) with the copolymers taking intermediate times, increasing with *para* content. It was found that the polymers could be dissolved in homogeneous MSA/CH₂Cl₂ mixtures of up to 80 % CH₂Cl₂. However, the mixture phase separated into an MSA/polymer-rich phase and a

CH_2Cl_2 /polymer lean phase when the solvent mixture was more than 50% CH_2Cl_2 .

The work-up procedure of the sulfonated polymers involves precipitation into water from strongly acidic medium. Some of the imine moieties of thiazole rings in the recovered sulfo PBTs were expected to be protonated as evidenced by the increased solubility and change of color when these polymers were dissolved in DMSO containing a small amount of ammonium hydroxide. Reddish solutions were obtained in pure DMSO, which changed to greenish brown upon the addition of base. All of the sulfo PBTs eventually dissolved in basic DMSO upon the application of heat (100 °C) with stirring. Films of *p*-sulfo PBT, cast from dilute neutral DMSO solutions are transparent, tough, and orange in color. Films cast from basic DMSO are opaque, yellow-green.

2-10 Thermal Stability

Thermogravimetric analyses of the sulfonated polymers, as shown in Table 2-3, confirm that thermal stability is largely retained in these polymers with onset temperatures typically near 500 °C.

Neither the incorporation of *meta* linkages in the polymer, nor the addition of a second sulfonate group, appears to have a dramatic effect upon thermal stability. The non-sulfonated *p*-PBT control compared well with the WPAFB standard *p*-PBT, showing good thermal stability. Both polymers retained 90 % or more of their original mass up to 730 °C. The sulfonated polymers all behaved similarly, losing less than 10% of their mass at ~500 °C, and subsequently thermally decomposing in two stages (Figure 2-12).

2-11 Birefringence Properties

Optical microscopy under crossed polarizers was used to investigate lyotropic behavior. *p*-PBT has been known to show liquid crystallinity in MSA

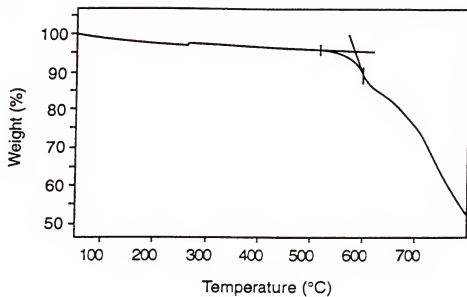
Table 2-3 Thermogravimetric analysis results of sulfo PBTs compared to non-sulfonated PBT.

Polymer	ID	<i>para</i> %	Onset temperature (°C)
<i>p</i> -sulfo PBT	<u>7a</u>	100	452
<i>p</i> -sulfo PBT	<u>7b</u>	100	580
<i>m</i> -sulfo PBT	<u>8a</u>	0	561
<i>p/m</i> -sulfo PBT	<u>9a</u>	75	542
<i>p/m</i> -sulfo PBT	<u>9b</u>	50	503
<i>p/m</i> -sulfo PBT	<u>9c</u>	25	496
<i>m</i> -disulfo PBT	<u>10</u>	0	500
<i>p</i> -PBT (control)	<u>11a</u>	100	714
<i>p</i> -PBT (WPAFB)	<u>11b</u>	100	749

solutions, and this was confirmed on the non-sulfonated *p*-PBT synthesized as a control. None of the sulfonated PBTs displayed lyotropicity under crossed polarizers in MSA. However, the *p*-sulfo PBT with highest viscosity, did exhibit birefringence when the sample was sheared between microscope slides. The WPAFB standard *p*-PBT formed a lyotropic solution with the 80/20 MSA/CH₂Cl₂ system down to a polymer concentration of 5%.

The all *para* sulfo PBT samples dissolved in basic DMSO exhibited lyotropicity at concentrations of 5 to 10%, which was retained upon removal of the ammonium hydroxide by heating. At concentrations between 2 and 5 %, birefringence could be induced by shear. A sample of *p*-sulfo PBT displayed spontaneous birefringence in 50/50 H₂O/DMSO at a concentration of 3%.

(a)



(b)

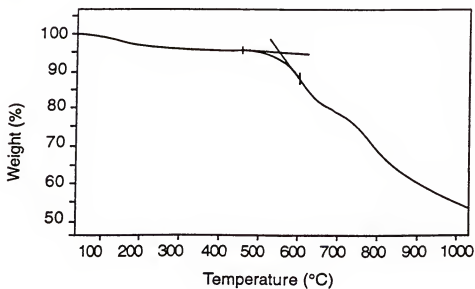


Figure 2-12 TGA diagrams of (a) *p*-sulfo PBT, (b) *m*-sulfo PBT, and (c) *m*-disulfo PBT compared with non-sulfonated (d) *p*-PBT control.

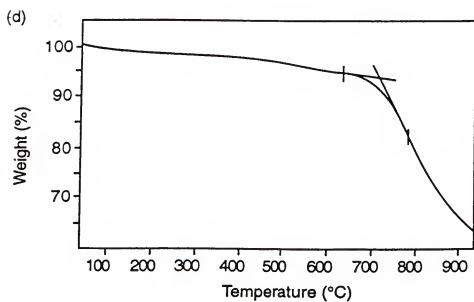
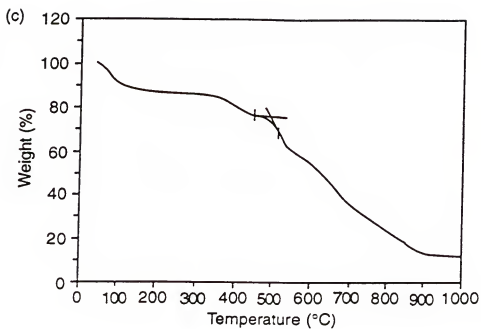


Figure 2-12 Continued.

2-12 Conclusions

Aromatic polyelectrolytes based on sulfonated PBTs have been synthesized and characterized. Control of polymerization reaction conditions, especially polymer concentration in solution, yields polymers exhibiting intrinsic viscosities of up to 3.0 dl/g for *p*-sulfo PBT. The incorporation of sulfonate groups onto the aromatic backbone increases solubility in organic solvents. All of the sulfonated PBTs dissolved well in basic DMSO. *m*-Disulfo PBT dissolves in water, alcohol, and strong acids. Two solvent systems, MSA/nitrobenzene and MSA/CH₂Cl₂ were found to be good solvents for both the sulfonated and non-sulfonated PBTs. With some modification, these solvent systems may lead to improved processing methods for these rigid-rod polymers. TGA results of all polymers show that sulfonated PBTs are highly thermally stable with onset temperatures for degradation over 500 °C. The *p*-sulfo PBT sample displayed birefringence in 50/50 H₂O/DMSO at a concentration of 3%.

CHAPTER 3

AROMATIC RIGID-ROD POLYELECTROLYTES BASED ON SULFONATOPROPOXY-SUBSTITUTED POLY(*p*-PHENYLENES)

3-1 Background of Sulfonatopropoxy-substituted PPPs Syntheses

As discussed in Section 1-6, non-substituted poly(*p*-phenylenes) (PPPs) are insoluble. PPPs with alkyl or alkoxy substituents have been developed using the Suzuki coupling method.^{5,48} These polymers are soluble in organic solvents such as toluene and chloroform, but insoluble in water.

Wallow and Novak⁵⁰ introduced the first water soluble PPP substituted with carboxylic acid functionalities. A water-soluble Pd(0) catalyst, Pd[P(C₆H₅)₂C₆H₄-*m*-SO₃⁻Na⁺]₃, was employed in order to use homogeneous coupling reaction conditions for the synthesis of the PPP with high molecular weight. Typical Pd(0) catalysts (i.e. Pd(PPh₃)₄) used for Suzuki coupling are organic soluble and thus employed in a heterogeneous reaction medium, such as a water/toluene mixture. The sodium salt of the polymer, poly(*p*-quaterphenylene-2,2'-dicarboxylic acid), is water-soluble and can be readily converted into insoluble, solvent resistant materials by either reprotonation with strong acid or ion-exchange with either Mg²⁺ or Zn²⁺.⁵³

The problem of polymer precipitation during polymerization has been discussed in Section 1-7. The carboxylated polymer does not precipitate out of the reaction medium due to its basicity converting the carboxylic acid-substituted PPP to sodium salt form.

With the background given above, our group targeted the synthesis of a new type of water-soluble PPP. The introduction of sulfonatopropoxy groups onto aromatic backbones has been of great interest in our group.^{9,10} The

sulfonatopropoxy group can improve water solubility of the resultant polymer without significant steric disruption of the polymer's conjugation.

Two polymers, specifically, poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-1,4-phenylene] sodium salt (PPP-OPSO₃), and poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene-*alt*-4,4'-biphenylene] sodium salt (PPBP-OPSO₃), have been the focus of this work. A water-soluble Pd(0) catalyst, Pd[P(C₆H₅)₂C₆H₄-*m*-SO₃⁻Na⁺]₃, was used for the syntheses of PPP-OPSO₃ which contains a biphenyl repeat unit, and PPBP-OPSO₃ which contains a terphenyl repeat unit. This catalyst easily loses its catalytic activity upon exposure to air as explained in Section 1-9. Recently Novak et al. reported a catalytic activity of Pd(OAc)₂ which is stable in air. They found this catalyst to be more useful than the water-soluble Pd(0) catalyst.⁶⁶ In this work, Pd(OAc)₂ has also been used for the syntheses of PPP-OPSO₃.

One important goal of this work is to obtain high molecular weight polymer. Since typical Suzuki coupling occurs under basic conditions, the effect of the reaction medium pH has been investigated as a parameter that controls the degree of polymerization. UV-Vis spectrophotometry has been used as an indirect method monitoring the effect of pH dependence on the degree of polymerization by measuring the energy of π - π^* absorption.

The measurement of molecular weights of water-soluble PPPs is difficult as Wallow and Novak have reported.^{50(b)} Gel permeation chromatography (GPC) is a typical method employed for the measurement of polymer molecular weights. However, the molecular weights of the new PPPs could not be determined using GPC because these polymers adsorbed on the GPC columns. Matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-MS) was attempted to obtain absolute molecular weights of the new water-soluble PPPs, however, the results were inconclusive. Colligative

methods, such as vapor phase osmometry and membrane osmometry (VPO and MO) were considered for the determination of number average molecular weights, but are not appropriate because the ionic PPPs contain counterions which are erroneously counted using this method.⁷¹ Light scattering would also prove difficult for measurement of weight average molecular weight because the PPPs are strongly fluorescent.⁷¹

Endgroup analysis using NMR spectroscopy or elemental analysis could not be directly employed because the water-soluble PPPs do not contain endgroups that can be quantitatively detected. However, terminating the chain ends with spectroscopically detectable groups (e.g. *t*-butyl) allows for the direct determination of degree of polymerization (X_n). The idea is to cap both chain ends of the polymer with a known group having a specific ^1H -NMR resonance. By comparing the number of hydrogens due to repeat units with those of endgroups, degrees of polymerization are calculated, yielding the number average molecular weight. Detailed calculations will be discussed later in this chapter.

One important characteristic of these sulfonatopropoxy-substituted PPPs is that they can be electrochemically oxidized and reduced. Optoelectrochemistry of PPP-OPSO₃ has been communicated by Child and Reynolds.⁶⁵ The polymer shows a band structure consistent with bipolaron charge carrier formation. This work indicated that the sulfonatopropoxy groups impart an electronic stabilizing effect on positive charge carriers.

In addition, luminescent properties of the new water-soluble PPPs have been applied to light emitting devices. Most luminescence studies on potential polymer-based light emitting devices have been developed using poly(phenylenevinylenes) (PPVs).^{59,60} However, the photoluminescence properties of PPPs have gained interest with the recent introduction of blue-

green light emitting devices based on PPP and poly(alkylfluorene).^{61,62} Therefore, luminescence studies on water-soluble PPPs (PPP-OPSO₃ and PPBP-OPSO₃) have been employed in this work. UV-Vis and fluorescence spectrophotometry have been employed to measure light absorption and emission for sulfonatopropoxy-substituted PPP derivatives. Photoluminescence and electroluminescence have been tested for PPP-OPSO₃/polyethyleneimine (PEI) multi-layers which were prepared by repeated electrostatic deposition in collaboration with Rubner et al.⁷² More experiments are being conducted using PPP-OPSO₃ in blue emitting devices.

As described above, these newly designed and synthesized PPPs have many interesting properties. Synthesis, characterization, and molecular weight determinations will be discussed in this chapter.

3-2 Results and Discussion

3-2-1 Monomer syntheses

Two different types of monomers, diboronic acids and disulfonatopropoxydibromobenzenes were used for the preparation of sulfonatopropoxy-substituted PPPs, PPP-OPSO₃, and PPBP-OPSO₃. Diboronic acids, 1,4-benzenediboronic acid, and 4,4'-biphenyldiboronic acid-(2,2'-dimethyl)propyl-diester, were synthesized according to literature procedure.⁷³

1,4-Benzenediboronic acid was synthesized using a Grignard reaction of 1,4-dibromobenzene with Mg turnings in THF (Figure 3-1 (a)). Trimethylborate was reacted with the Grignard reagent, leaving 1,4-benzenebis(dimethylborate) (**1**) as a precipitate. The precipitate was reacted with an aliquot of 20 % sulfuric acid. The crude 1,4-benzenediboronic acid (**2**) was extracted from ether and purified by recrystallization from boiling water.

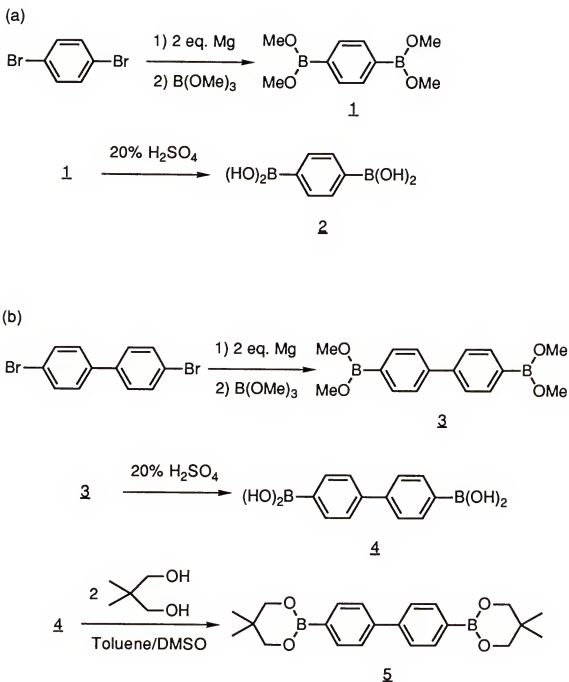


Figure 3-1 Synthetic routes for (a) 1,4-benzenediboronic acid and (b) 4,4'-biphenyldiboronic acid-(2,2'-dimethyl)propyldiester.

4,4'-Biphenyldiboronic acid (2,2'-dimethyl)propyldiester was synthesized via Grignard reaction of 4,4'-dibromobiphenyl with Mg turnings in dry THF (Figure 3-1 (b)). Trimethylborate was reacted with the Grignard reagent, leaving 4,4'-biphenylbis(dimethylborate) (**3**) precipitate. The precipitate was treated with 20 % aqueous sulfuric acid. The crude 4,4'-biphenyldiboronic acid (**4**) was extracted from ether. The crude diboronic acid was converted to boronic acid diester (**5**) via esterification with 2,2'-dimethyl-1,3-propanediol.

Obtaining completely anhydrous 1,4-benzenediboronic acid was tedious because diboronic acids are typically obtained as monohydrates. The aromatic diboronic acids tend to lose water when heated *in vacuo* at temperatures above 230 °C and result in polymeric anhydrides that do not melt below 400 °C. The 1,4-benzenediboronic acid collected by filtration was gently heated at 60 °C to remove water and prevent anhydride formation. ¹H-NMR in 100 % D₂O still showed a small water content in the 1,4-benzenediboronic acid after drying, but was used since 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene, contains water due to the hygroscopic sulfonate groups.

The necessary formation and use of 4,4'-biphenyldiboronic acid (2,2'-dimethyl)propyldiester in place of 4,4'-biphenyldiboronic acid resulted from a purity problem of the acid which could not be purified by recrystallization in any solvent including water. The ester derivative of the diboronic acid could be crystallized in DMSO/toluene mixture. Finally highly pure 4,4'-biphenyldiboronic acid (2,2'-dimethyl)propyldiester was obtained and used for polymerization.

1,4-Dibromo-2,5-di(3-sulfonatopropoxy)-benzene disodium salt was synthesized according to the procedure developed in our group as shown in Figure 3-2 (Personal communication with J. Dharia). 1,4-Dimethoxybenzene, used as starting material, was reacted with bromine to produce 1,4-dibromo-

2,5-dimethoxybenzene (**6**). Boron tribromide was used for the methylether cleavage of 1,4-dibromo-2,5-dimethoxybenzene. Hydrolyzed product, 1,4-dibromohydroquinone (**Z**), was reacted with 1,3-propanesultone to form 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene (**8**).

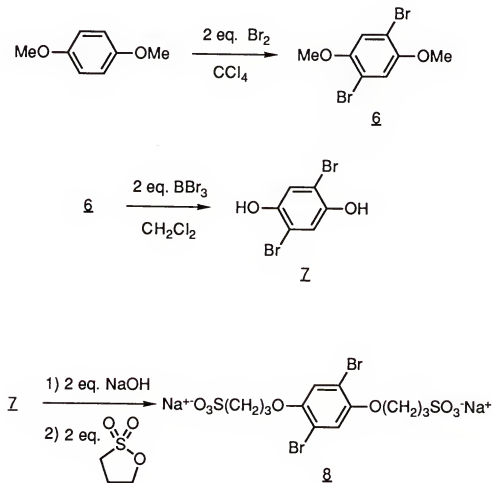


Figure 3-2 Synthetic route for 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene.

Dibromination of 1,4-dimethoxybenzene in CCl_4 was the first step for the synthesis of 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene. No catalyst was necessary, but the bromination was facilitated by an effective liberation of HBr gas released from the reaction. Saturated aqueous NaOH was used to collect and neutralize the HBr gas. During synthesis of the 1,4-dibromo-2,5-dimethoxybenzene precipitated out. After neutralization of the CCl_4 solution

using aqueous K_2CO_3 , the rest of the 1,4-dibromo-2,5-dimethoxybenzene was recovered and recrystallized from EtOH.

The reaction of boron tribromide with 1,4-dibromo-2,5-dimethoxybenzene in CH_2Cl_2 to cleave the ethers was straightforward, however, the reaction turned yellow-brown upon exposure to air.

1,4-Dibromohydroquinone was readily reacted with NaOH in EtOH under argon atmosphere. The reaction turned yellow to orange by adding NaOH. However, it turned brown when exposed to air, which caused a color impurity that could not be removed.

The use of a 10 % excess of NaOH, and 5 % excess of 1,3-propanesultone, during the disulfonate synthesis was effective for removing unreacted 1,3-propanesultone by converting it into water-soluble 3-hydroxypropyl-sulfonate sodium salt. After recrystallization from water, other water-soluble impurities were removed.

3-2-2 Synthesis of Water-soluble Pd(0) Catalyst

A water soluble Pd(0) catalyst, $(Pd[P(C_6H_5)_2C_6H_4-m-SO_3Na]_3)$, was synthesized according to a literature procedure⁵⁰ (Figure 3-3). Diphenylphosphinobenzene-*m*-sulfonic acid sodium salt (9) was synthesized via sulfonation of triphenylphosphine with 27-33 % fuming sulfuric acid followed by neutralization with aqueous NaOH. (Note: The diphenylphosphinobenzene-*m*-sulfonic acid sodium salt can now be purchased from TCI America.) The synthesized diphenylphosphinobenzene-*m*-sulfonic acid sodium salt was subsequently reacted with $PdCl_2$ in DMSO. Treatment of the reaction with hydrazine reduced the palladium complex to produce tris(diphenylphosphinobenzene-*m*-sulfonic acid)palladium(0) sodium salt (10). The final product was recrystallized from EtOH. The reaction was carried out under an

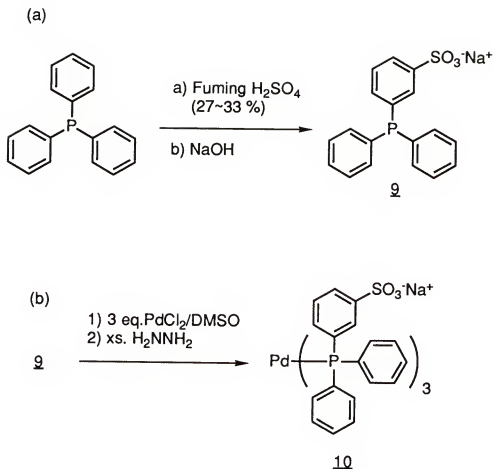


Figure 3-3 Synthetic routes for (a) sulfonation and (b) Pd(0) complex formation. inert atmosphere to prevent the Pd(0) complex from oxidizing in air.

The sulfonation step for the synthesis of diphenylphosphinobenzene-*m*-sulfonic acid sodium salt was not easily controlled because an excess of fuming sulfuric acid is used for the monosulfonation. Prevention of disulfonation or trisulfonation was important. Aliquots were taken from the sulfonation reaction periodically to perform solubility tests in water with the assumption that monosulfonated triphenylphosphine dissolves in water, while unreacted triphenylphosphine precipitates. When the aliquots did not subsequently precipitate, the reaction was immediately quenched in cold water. The reaction was unpredictable with slow heating at a relatively low temperature (ca. 50 °C)

at the beginning of the reaction being most effective for reaction control. Recrystallization of the final product from water could not be carried out when the triphenylphosphine was oversulfonated.

Neutralization was carried out after the monosulfonation. White shiny powder was released from the solution when neutralized with aqueous NaOH. However, at pH greater than 7, the product turned off-white. Precise pH control for neutralization was important to obtain pure monosulfonated product. Recrystallization of the product from water was carried out with temperature control. The temperature had to be equal or higher than room temperature because Na_2SO_4 precipitates from the solution via neutralization at 0 °C.

The water-soluble Pd(0) complex was much more air-sensitive than other common Pd(0) complexes such as tetrakis(triphenylphosphine)palladium. Its synthesis was carried out in an inert atmosphere. PdCl_2 dissolved very slowly in DMSO at elevated temperature (ca. 100 °C). After the injection of hydrazine via canula into the reaction, the reduced Pd(0) complex appeared as a bright yellow powder. The Pd(0) complex was filtered, recrystallized, and dried using a three neck flask equipped with medium glass filter in one of the necks under argon. This limited, but did not completely prevent exposure to air. The best way to avoid air-exposure is to carry out all experiments in a drybox equipped with a filtration apparatus and vacuum oven.⁵¹ The Pd(0) catalyst slowly loses its bright yellow color under ordinary fluorescent light. Therefore, light protection was necessary before use.

Because of the air-sensitivity of the water-soluble Pd(0) catalyst, a different type of Pd catalyst compatible to the water-soluble Pd(0) catalyst was considered. Coupling reactions using $\text{Pd}(\text{OAc})_2$ were reported to be faster than the Pd(0) catalyst because the triphenylphosphine groups in the Pd(0) catalyst are known to retard the coupling reaction.^{55(b),66} $\text{Pd}(\text{OAc})_2$ is stable to air-

and light-exposure. One important comparison is that the $\text{Pd}(\text{OAc})_2$ is insoluble in water, while tris(diphenylphosphinobenzene-*m*-sulfonic acid)palladium(0) sodium salt is water-soluble. These differences in catalyst solubility and reactivity motivated a catalytic activity comparison in this work between $\text{Pd}(\text{OAc})_2$ and the water-soluble $\text{Pd}(0)$.

3-2-3 Synthesis of Model Compound

3-2-3-1 Model compound synthesis results

The model compound, 2,5-diphenyl-1,4-(2-sulfonatopropoxy)benzene sodium salt (**11**) was synthesized as a structural model of the coupling reaction between water-soluble diboronic acid and dibromide monomers (Figure 3-4). Tris(diphenylphosphinobenzene-*m*-sulfonic acid)palladium(0) sodium salt and $\text{Pd}(\text{OAc})_2$ were used as a catalyst, respectively. The same synthetic conditions that were used for the synthesis of PPP-OPSO₃ and PPBP-OPSO₃ were employed for the syntheses of the model compound.

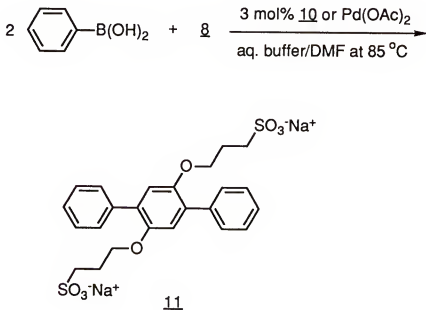


Figure 3-4 Synthetic route for model compound, 2,5-diphenyl-1,4-(2-sulfonatopropoxy)benzene sodium salt.

Benzeneboronic acid was used as received. 1,4-Dibromo-2,5-di(3-sulfonatopropoxy)benzene was synthesized following the procedure detailed in experimental section (Section 3-3). A mixture of 70 % aqueous 0.2 M Na_2CO_3 with 30% DMF was used as solvent. The solvent was deaerated before use to prevent the loss of Pd(0) catalytic activity. The reaction was carried out at 85 °C under argon.

In the model compound synthesis, the catalytic activity of the two different Pd catalysts were compared to each other. Reaction rates could be detected by the color change of the reaction as Pd particles precipitated when the reaction neared completion.

3-2-3-2 Characterization of 2,5-diphenyl-1,4-(2-sulfonatopropoxy)benzene sodium salt

The structure of the model compound was characterized using ^1H - and ^{13}C -NMR spectroscopy. As shown in Figure 3-5, the 1:1 integral ratio of aromatic hydrogens to aliphatic hydrogens in the ^1H -NMR is consistent with the model compound, carrying two sulfonatopropoxy groups. The presence of the strong peaks at 138.36 and 150.54 ppm in the ^{13}C -NMR spectrum clearly proved the formation of the aryl linkage (Figure 3-6). All peaks were assigned for each specific carbon. Elemental analysis results were in good agreement with theoretical values.

The FT-IR spectrum of the model compound proved the existence of two strong absorption bands indicating asymmetric and symmetric S=O stretching of sulfonate group found at 1205 and 1047 cm^{-1} (Figure 3-7). Also aliphatic C-H stretching due to propyl group was found at 2952 and 2874 cm^{-1} , while aromatic C=C stretching of benzene ring was found at 1635-1655 cm^{-1} and aromatic C-H of benzene ring at 3033 cm^{-1} .

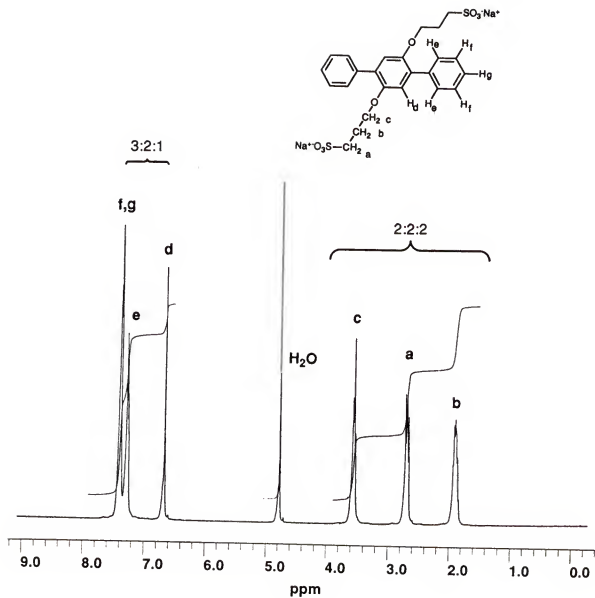


Figure 3-5 ^1H -NMR spectrum of model compound.

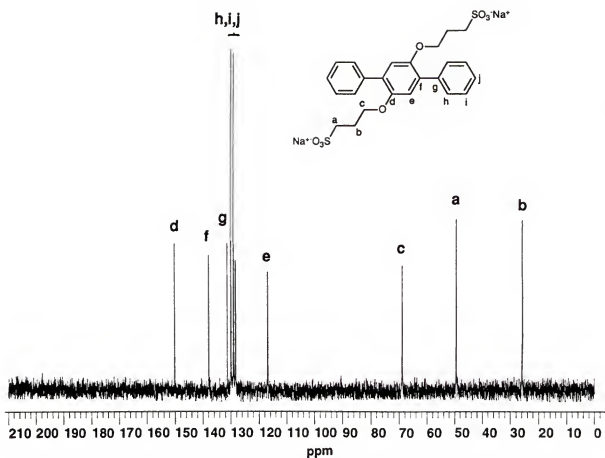


Figure 3-6 ^{13}C -NMR spectrum of model compound.

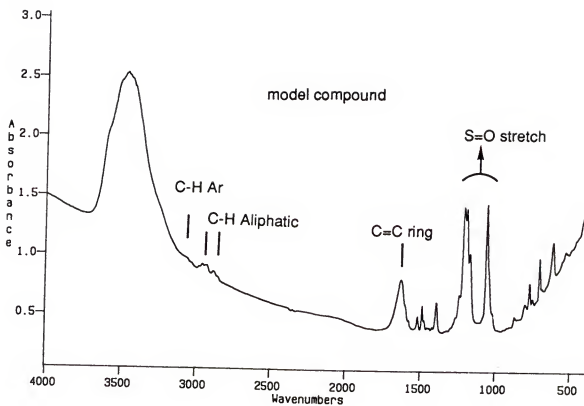


Figure 3-7 FT-IR spectrum of model compound.

The λ_{max} of the π - π^* absorption in the UV-Vis spectrum in aqueous solution was detected at (4.1 eV, 305 nm) higher than the value (4.5 eV, 276 nm) for unsubstituted terphenyl.⁷⁴ Steric interactions of the sulfonatopropoxy substituents would make the compound less planar than the unsubstituted terphenyl and a blue shift in the absorption could be expected. However, the UV-Vis results indicate that a red shift (276 to 305 nm) occurs by the addition of the sulfonatopropoxy groups on the center phenylene backbone. The electron-donating effect of the propoxy substituents would counterbalance the blue shift and overcompensate for the steric effect. This will be of importance later when considering polymer spectra.

3-2-4 Polymer Syntheses

3-2-4-1 Polymerization results

All polymerizations, as illustrated in Figure 3-8, were run using the reaction conditions outlined in the experimental section. Mixtures of 70 % aqueous base with different pHs (8.0, 10.0, 12.0) with 30 % DMF were prepared as solvents for the polymerization. This combination was initially used as a solvent for the water-soluble PPP with dicarboxy substituents synthesized by Wallow and Novak because relatively low basic conditions (ca. pH 7.8) were believed to prevent aryl exchange products which causes a defect in the rigid-rod structure of PPP.⁵⁰ However, sufficient basicity for the hydrolysis step is very important for increasing the solubility of the boronic acid monomer for the coupling reaction.

The solution pH affects the polymerization rate especially when a diboronic ester monomer, such as 4,4'-biphenyldiboronic acid-(2,2'-dimethyl)propylester, was used. Therefore, the purpose of a pH dependence investigation is to achieve homogeneous reaction conditions to obtain high

polymer. Another important factor is the pH dependence of catalytic activity that may affect molecular weight.

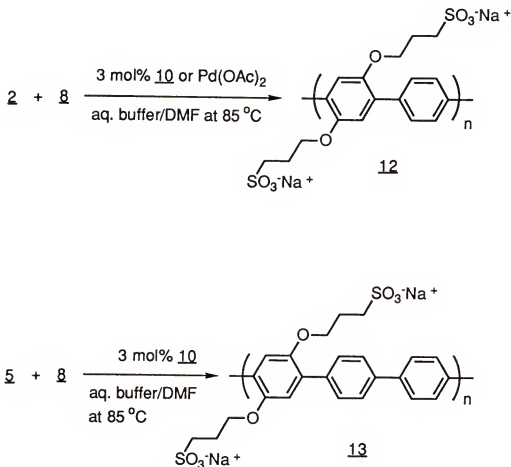


Figure 3-8 Synthetic routes for PPP-OPSO₃ and PPBP-OPSO₃.

For this purpose, aqueous solutions with three different pHs (8.0, 10.0, and 12.0) were prepared by mixing 0.2 M NaHCO₃/0.2 M AcOH, 0.2 M NaHCO₃/0.2 M Na₂CO₃, and 0.2 M NaCO₃/0.1 M NaOH respectively.

The syntheses of PPP-OPSO₃ (**12**) polymers were performed using the reaction conditions outlined in the experimental section. Typically, reactions were heated at 85-90 °C for 24 hours regardless of which type of catalyst was used. The precipitated Pd particles were removed by filtration using medium glass filter.

The syntheses of PPBP-OPSO₃ (13) polymers were run using the reaction conditions outlined in the experimental section. For this reaction, the water-soluble Pd(0) complex was used as catalyst because the diboronic ester monomer, 4,4'-biphenyldiboronic acid (2,2'-dimethyl)propyldiester, was insoluble in the aqueous buffer solvent mixture in the initial stages of the coupling reaction. The monomer was slowly dissolved as it hydrolyzed. Therefore, an overall slow polymerization rate was expected to be better controlled by the catalyst with a lower activity. Typically reactions were heated at 85-90 °C for 24 hours. The precipitated Pd particles were removed by filtration using a medium glass filter.

The catalytic activity of the two different Pd catalysts were compared against each other for the polymerization. Reaction rates could be detected by monitoring fluorescence of the reaction under a UV lamp. The reactions using Pd(OAc)₂ were found to be significantly faster than that using water-soluble Pd(0) catalyst. After removal of Pd particles by filtration, the filtrate turned tan-violet color. The dialyzed polymer products were soluble only in water.

3-2-4-2 Characterization of polymers

The structure of PPP-OPSO₃ was determined using ¹H- and ¹³C-NMR spectroscopy. As shown in Figure 3-9 (a), all peaks in the ¹H-NMR spectrum using D₂O were broad. The spectrum did not give any information of endgroups. However, the 2:1 integral ratio for the two different aromatic hydrogens as expected for the polymer repeat unit. Three different peaks for aliphatic hydrogens in the ¹H-NMR indicates that the PPP-OPSO₃ carrying two sulfonatopropoxy groups per repeat unit was successfully synthesized. The ¹³C-NMR spectrum shows each carbon peak clearly. The presence of strong peaks at 137.98 and 150.79 ppm in the ¹³C-NMR spectrum clearly proved the

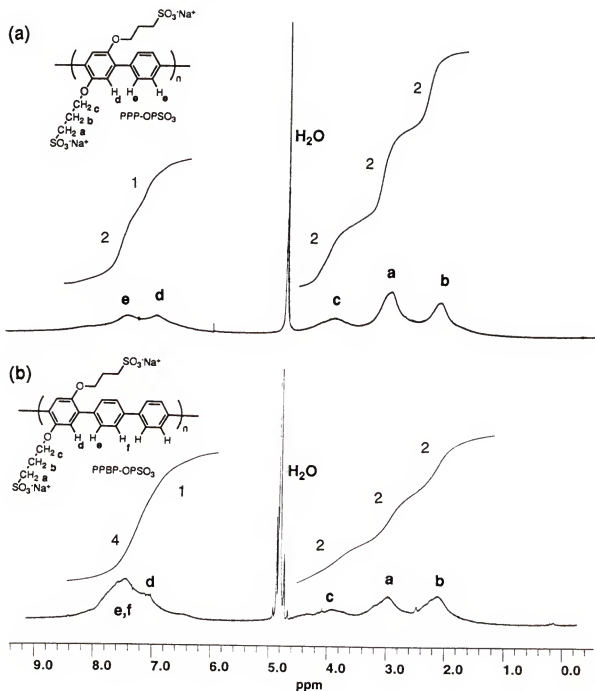


Figure 3-9 ^1H -NMR spectra of (a) PPP-OPSO₃ and (b) PPBP-OPSO₃.

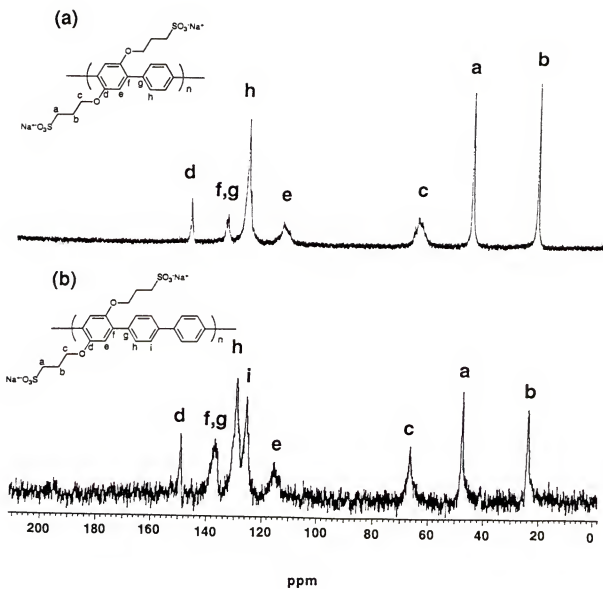


Figure 3-10 ^{13}C -NMR spectra of (a) PPP-OPSO₃ and (b) PPBP-OPSO₃.

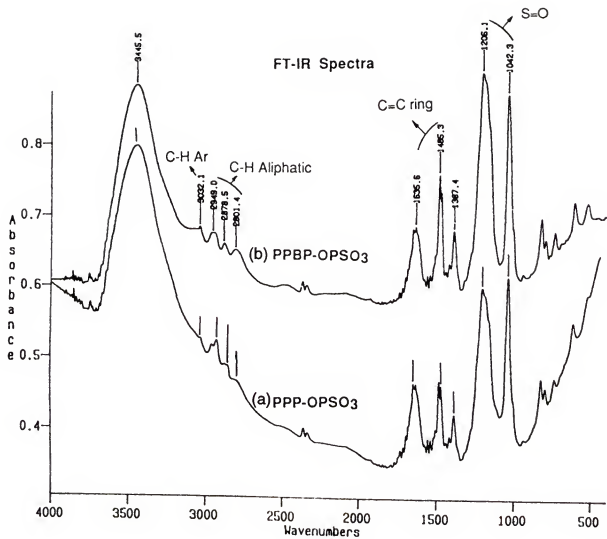


Figure 3-11 FT-IR spectra of (a) PPP-OPSO₃ and (b) PPBP-OPSO₃.

formation of the aryl linkage (Figure 3-10 (a)). All the carbons were assigned according to the carbon peak positions.

The structure of PPBP-OPSO₃ was also characterized using ¹H- and ¹³C-NMR spectroscopy. Figure 3-9 (b) shows that all peaks in the ¹H-NMR spectrum in D₂O are broad. The 4:1 integral ratio for two different aromatic hydrogens is as expected for the polymer repeat unit. Three different peaks for aliphatic hydrogens in the ¹H-NMR indicates that the PPBP-OPSO₃ was successfully synthesized without a loss of alkyl sulfonate groups. The ¹³C-NMR spectrum shows each carbon peaks clearly. All of the carbons were assigned according to the carbon peak positions (Figure 3-10 (b)).

There was no significant difference between the FT-IR spectra of PPP-OPSO₃ and PPBP-OPSO₃ (Figure 3-11). The FT-IR spectra of PPP-OPSO₃ and PPBP-OPSO₃ proved the existence of two strong absorption bands indicating asymmetric and symmetric S=O stretching of sulfonate groups found at 1185-1210 and 1040-1050 cm⁻¹ range. Also, aliphatic C-H stretching vibrations of propyl groups were found at 2935-2940, 2875-2880, and 2800-2805 cm⁻¹, while aromatic C=C stretch of benzene rings was at 1635-1645 cm⁻¹ and aromatic C-H of benzene rings at 3030-3040 cm⁻¹.

The elemental analysis results are not in good agreement with calculated values as shown in the experimental section.

3-2-4-3 UV-Vis spectra and their application to pH dependence of polymerization

The UV-Vis spectra of PPP-OPSO₃ and PPBP-OPSO₃ synthesized at different pHs (8.0, 10.0, and 12.0) were obtained in aqueous solutions. The UV-Vis spectra were taken in order to monitor the bathochromic shift during the formation of the polyphenylene linkages. The other important reason is that the λ_{\max} measurement of the π - π^* absorptions of these polymers could be used as

a tool to indirectly monitor degrees of polymerization according to different aqueous pH conditions, assuming that increasing degrees of polymerization may result in a small red-shift. The results are summarized in Table 3-1.

As shown in Table 3-1, The λ_{\max} of the $\pi-\pi^*$ absorption for the PPP-OPSO₃ was found between 339-342 nm under different pH conditions when the water-soluble Pd(0) complex was used. The results are similar to the λ_{\max} of the $\pi-\pi^*$ absorption for the PPP-OPSO₃ when Pd(OAc)₂ was employed at pH 10.0 and 12.0. However, the λ_{\max} value of the $\pi-\pi^*$ absorption at pH 8.0 was lower than those at the other pHs (10.0 and 12.0).

Table 3-1 pH dependence of polymerization monitored by the λ_{\max} of $\pi-\pi^*$ absorption for PPP-OPSO₃ and PPBP-OPSO₃.

Polymer samples	Pd catalyst	pH of aqueous buffer	λ_{\max} of $\pi-\pi^*$ absorption
PPP-OPSO ₃ (12a)	Pd(0) complex	8.0	339 nm
PPP-OPSO ₃ (12b)	Pd(0) complex	10.0	339 nm
PPP-OPSO ₃ (12c)	Pd(0) complex	12.0	342 nm
PPP-OPSO ₃ (12d)	Pd(OAc) ₂	8.0	329 nm
PPP-OPSO ₃ (12e)	Pd(OAc) ₂	10.0	341 nm
PPP-OPSO ₃ (12f)	Pd(OAc) ₂	12.0	339 nm
PPBP-OPSO ₃ (13a)	Pd(0) complex	8.0	---
PPBP-OPSO ₃ (13b)	Pd(0) complex	10.0	352 nm
PPBP-OPSO ₃ (13c)	Pd(0) complex	12.0	349 nm

It is interesting that PPBP-OPSO₃ was not obtained at pH 8.0. As explained above, the diboronic ester monomer, 4,4'-biphenyldiboronic acid(2,2'-dimethyl)propyldiester, is slightly soluble in the aqueous buffer solvent indicating that relatively strong basic conditions are required when the diboronic ester is used as the monomer. PPBP-OPSO₃ showed a bathochromic shift to 349-352 nm when the polymerization was carried out at pH was at 10.0 and 12.0. Comparison of PPBP-OPSO₃ to the PPP-OPSO₃ indicates that the less substituted PPBP-OPSO₃ has more highly extended conjugation per repeat unit as evidenced by a further red shift.

Each sample of PPP-OPSO₃ polymer (except 12d) showed 4 absorption peaks (205, 238-239, 287-288, 339-342 nm) in the UV range (Figure 3-12). Rice and Gartstein⁷⁵ recently reported a charge conjugation symmetry breaking theory of substituted PPP by showing theoretical absorption bands caused by conjugation. Our experimental values are identical to the theoretical values calculated using their theory. This theory claims that four excitation bands ($E_{1u}(x)$, $E_{1u}(y)$, B_{1u} , and B_{2u}) of the benzene ring modified by polymerization exist by combining three factors, the primary excitation of phenylene monomer, the correlation energy gap between charged and charge-neutral excitation, and the dipole-dipole interaction between local excitations on neighboring monomers. By following this theory, the two bands at approximately 3.6 and 6.0 eV are the low energy and high energy components of the excitations derived from the $E_{1u}(x)$ excitation of benzene and are polarized along the polymer axis. The bands at approximately 5.2 and 4.3 eV correspond to the excitations derived from the $E_{1u}(y)$ and B_{2u} excitations of benzene, respectively, and are polarized perpendicular to the polymer axis. The PPP spectra confirm the presence of the $E_{1u}(y)$ derived by this theory. Moreover, the B_{2u} band is allowed when the charge conjugation symmetry of

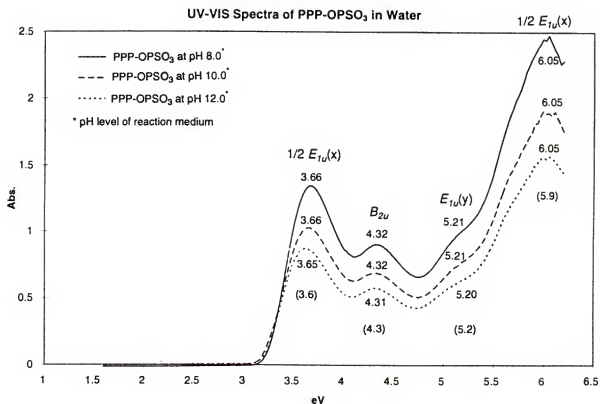


Figure 3-12 UV-Vis spectra of PPP-OPSO₃ illustrating the 4 different absorption bands. The numbers in parenthesis are theoretical values calculated by the charge conjugation symmetry breaking theory.

the unsubstituted PPP is broken by the addition of substituents. On the other hand, B_{1U} is forbidden.

3-2-4-4 Fluorescence properties in aqueous solution

Fluorescence spectra of aqueous solutions of PPP-OPSO₃ and PPBP-OPSO₃ were taken. The UV exposure of the PPBP-OPSO₃ and PPBP-OPSO₃ polymer samples in aqueous solution resulted in bright blue light emission indicative of their fluorescence properties as summarized in Table 3-2.

Table 3-2 Fluorescence spectral results of PPP-OPSO₃ and PPBP-OPSO₃.

Polymer samples	Pd catalyst	λ_{\max} of fluorescent light
PPP-OPSO ₃ (12a)	Pd(0) complex	420 \pm 10 nm
PPP-OPSO ₃ (12b)	Pd(0) complex	420 \pm 10 nm
PPP-OPSO ₃ (12c)	Pd(0) complex	420 \pm 10 nm
PPP-OPSO ₃ (12d)	Pd(OAc) ₂	420 \pm 10 nm
PPP-OPSO ₃ (12e)	Pd(OAc) ₂	420 \pm 10 nm
PPP-OPSO ₃ (12f)	Pd(OAc) ₂	420 \pm 10 nm
PPBP-OPSO ₃ (13a)	Pd(0) complex	----
PPBP-OPSO ₃ (13b)	Pd(0) complex	420 \pm 10 nm
PPBP-OPSO ₃ (13c)	Pd(0) complex	420 \pm 10 nm

The maximum emission of PPP-OPSO₃ and PPBP-OPSO₃ occurs at 420 \pm 10 nm, causing these polymers to be blue emitters. It should be noted that the PPP-OPSO₃ samples synthesized under different aqueous pH conditions have different UV absorptions, but their λ_{\max} for emission are close to each other.

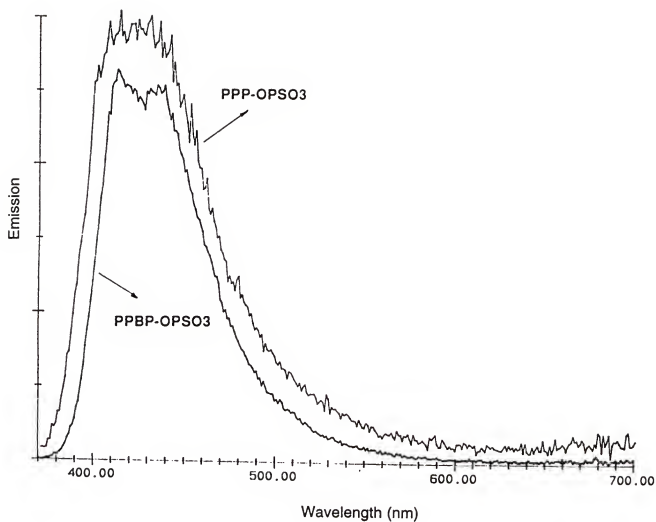


Figure 3-13 Fluorescence spectra of (a) PPP-OPSO₃ and (b) PPBP-OPSO₃.

The fluorescence spectra of PPP-OPSO₃ and PPBP-OPSO₃ are compared in Figure 3-13.

3-2-4-5 Thermal stability

Thermogravimetric analyses for the PPP-OPSO₃ and PPBP-OPSO₃ polymer samples were carried out and the results are summarized in Table 3-3.

Table 3-3 Thermogravimetric analyses results of PPP-OPSO₃ and PPBP-OPSO₃.

Polymer samples	Pd catalyst	Onset decomposition temperature (°C)
PPP-OPSO ₃ (12a)	Pd(0) complex	354
PPP-OPSO ₃ (12b)	Pd(0) complex	306
PPP-OPSO ₃ (12c)	Pd(0) complex	358
PPP-OPSO ₃ (12d)	Pd(OAc) ₂	338
PPP-OPSO ₃ (12e)	Pd(OAc) ₂	360
PPP-OPSO ₃ (12f)	Pd(OAc) ₂	360
PPBP-OPSO ₃ (13a)	Pd(0) complex	---
PPBP-OPSO ₃ (13b)	Pd(0) complex	378
PPBP-OPSO ₃ (13c)	Pd(0) complex	301

These results indicate that the polymer to be stable to ca. 300-350 °C in nitrogen. A significant weight loss (20~30 %) after the onset of decomposition temperatures occurred due to the loss of the sulfonatopropyl groups.

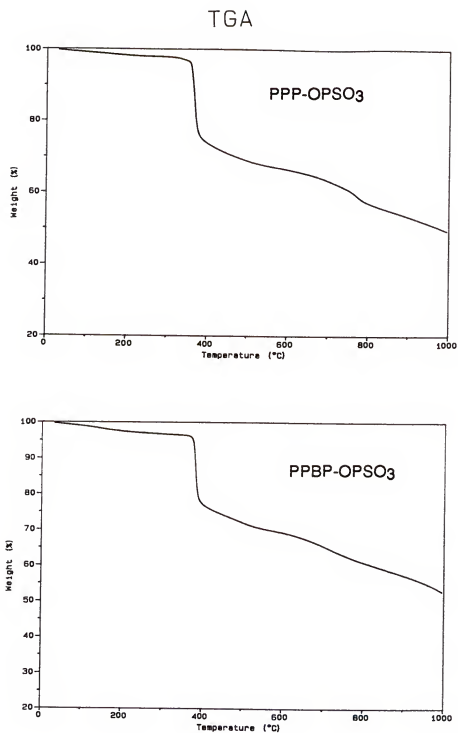


Figure 3-14 TGA results of PPP-OPSO₃ and PPBP-OPSO₃.

3-2-5 Molecular Weight Analysis Using Endgroup Capping Methodology

3-2-5-1 Background of endcapping method application

An important, yet difficult, question concerning this work is how molecular weight can be calculated for water-soluble PPPs. Wallow and Novak reported an approximate molecular weight (M_w) of their water-soluble polymer, poly(*p*-quaterphenylene-2,2'-dicarboxylic acid), relative to single-stranded DNA using poly(acrylamide) gel electrophoresis. However, they also reported that it is unreasonable to expect this method to give an accurate molecular weight, since the polymer is more rigid than single-stranded DNA in the absence of an absolute reference.

Gel permeation chromatography (GPC) was attempted to measure the molecular weight of PPP-OPSO₃ in an aqueous system. However, no results could be obtained since the polymer samples adsorbed on columns used. Matrix assisted laser desorption/ionization-mass spectroscopy (MALDI-MS) was attempted, but the result proved inconclusive.

At this point, end group analysis by capping the chain with a known end group was investigated because the number average molecular weight (M_n) could be directly measured if appropriate capping could be accomplished. In the polymerization, 4-*t*-butylbenzeneboronic acid (**14**) was used as an end capping reagent to produce 4-*t*-butylphenyl-endcapped PPP-OPSO₃ polymers (**15**) (TBPPP-OPSO₃) as shown in Figure 3-15.

The strategy to calculate X_n using the endcapping method is as follows. ¹H-NMR spectra of these polymers were taken and the numerical integral value of each proton calculated. By dividing the numerical integral value of the repeat unit propyl groups by that of the chain end *t*-butyl groups, the average degrees of polymerization were obtained. The number average molecular weight including end capping groups were then calculated.

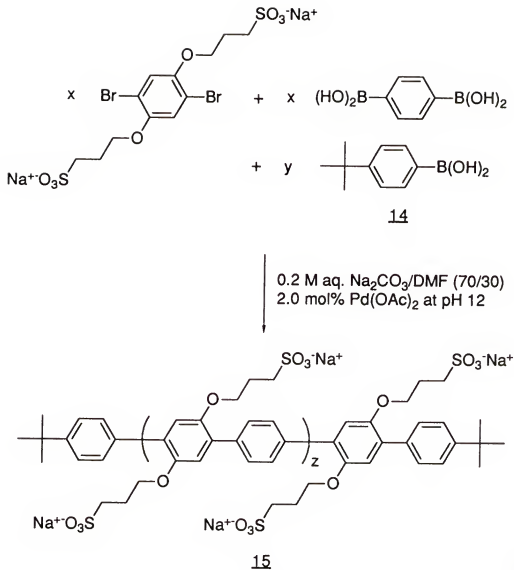


Figure 3-15 Synthetic route of TBPPP-OPSO₃.

3-2-5-2 Molecular weight control by endcapping⁷⁶

In order to properly control the polymer molecular weight, the stoichiometric imbalance of bifunctional monomers (A-A or B-B) can be adjusted, or the addition of a monofunctional monomer (A) can be used to introduce stoichiometric imbalance. In these experiments, A-A is equal to 1,4-dibenzeneboronic acid, A to 4-*t*-butylbenzeneboronic acid, and B-B to 1,4-

dibromo-2,5-(3-sulfonatopropoxy)benzene. With the addition of small amounts of a monofunctional reagent, stoichiometric imbalance r is defined as

$$r = \frac{N_{B-B}}{N_{A-A} + 2N_A}$$

where N_{A-A} is the number of $B(OH)_2$ functional groups in 1,4-dibenzene boronic acid, N_A is the number of $B(OH)_2$ functional groups in 4-*t*-butylbenzene boronic acid, and N_{B-B} is the number of Br in 1,4-dibromo-2,5-(3-sulfonatopropoxy)benzene.⁷⁶ It should be noted that $0 < r < 1$.

The number average degree of polymerization X_n is the total number of polymer units, or A-A and B-B molecules initially present divided by the total number of polymer molecules.

$$X_n = \frac{1+r}{1+r-2rp}$$

Here, p = the fractional extent of reaction of the functional groups. With the assumption that the polymerization is 100% complete ($p=1$), X_n can be defined as follows:

$$X_n = \frac{1+r}{1-r}$$

Assuming that N_{A-A} is equal to N_{B-B} , and the stoichiometric imbalance r is due to monofunctional reagent, r can be defined as

$$r = \frac{N_{A-A}}{N_{A-A} + 2N_A} = \frac{1}{1 + 2N_A/N_{A-A}}$$

The mole ratio can be converted to concentration by $(C_A \times A_N)/(C_{A-A} \times A_N)$ where A_N is Avogadro's number. Therefore, the stoichiometric imbalance r can

be calculated based on the concentrations of monomers and monofunctional reagent.

$$r = \frac{1}{1 + 2N_A/N_{A-A}} = \frac{1}{1 + C_A/C_{A-A}}$$

3-2-5-3 Experimental X_n control

Monofunctional monomer, 4-*t*-butylbenzeneboronic acid (**14**), was synthesized using 4-*t*-butylphenylmagnesium bromide. The 4-*t*-butylphenylmagnesium bromide was reacted with trimethyl borate. The 4-*t*-butylbenzeneboronic acid was obtained by hydrolysis of the borate product with 2 M aqueous HCl solution. Polymerizations with theoretical $X_n=3, 6, 9, 15, 17, 23, 35$ and 50, were run under the same reaction conditions used for the syntheses of PPP-OPSO₃.

TBPPP-OPSO₃ polymers were synthesized and their molecular weights were controlled by stoichiometric imbalance by addition of endcapping reagent, 4-*t*-butylbenzeneboronic acid. Figure 3-16 shows a typical ¹H-NMR used to obtain numerical integral values for comparison of repeat unit propyl protons with terminal *t*-butyl protons.

Assuming that the degree of polymerization is inversely proportional to the numerical integral values of the *t*-butyl groups on both polymer chain ends, the experimental degree of polymerization (X_n) can be defined as follows.

$$X_n = \frac{I(C_3H_6)}{I(t-C_4H_9)} \times \frac{9}{6} - 1$$

where $I(C_3H_6)$ is the numerical integral of the propyl group and $I(t-C_4H_9)$ is the numerical integral of the *t*-butyl group. The subtraction of 1 from the above

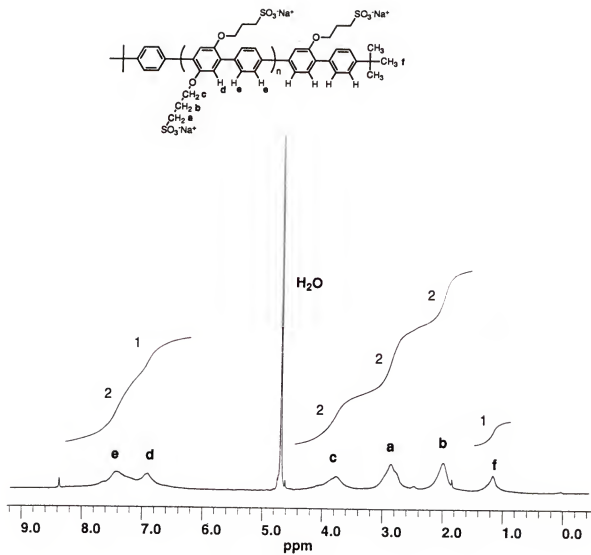


Figure 3-16 ¹H-NMR spectrum of TBPPP-OPSO₃ with $X_n=9$.

Table 3-4 Experimental X_n calculation results compared with theoretical X_n and monitored by the λ_{\max} of $\pi-\pi^*$ absorption for TBPPP-OPSO₃.

Polymer samples	Theoretical X_n	Experimental X_n	λ_{\max} of $\pi-\pi^*$ absorption
TBPPP-OPSO ₃ (15a)	3.0	4.0	323 nm
TBPPP-OPSO ₃ (15b)	6.0	7.4	329 nm
TBPPP-OPSO ₃ (15c)	9.0	7.7	330 nm
TBPPP-OPSO ₃ (15d)	12.0	12.4	330 nm
TBPPP-OPSO ₃ (15e)	17.0	17.1	333 nm
TBPPP-OPSO ₃ (15f)	23.0	17.5	333 nm
TBPPP-OPSO ₃ (15g)	35.0	32.2	336 nm
TBPPP-OPSO ₃ (15h)	50.0	41.9	338 nm

equation is necessary because TBPPP-OPSO₃ has one more equivalent propyl group per polymer chain (Refer to Figure 3-15).

Experimental results are summarized in Table 3-4 and compared with theoretical calculations. The λ_{\max} values of the TBPPP-OPSO₃ $\pi-\pi^*$ absorption were measured using UV-Vis spectroscopy. These values can be used as a standard to predict the minimum degree of polymerization for PPP-OPSO₃.

3-2-5-4 Analyses of experimental X_n calculation

All peaks shown in the ¹H-NMR spectra of TBPPP-OPSO₃ are broad. Experimental X_n calculations were carried out for 8 different TBPPP-OPSO₃ samples. The X_n results show a plausible approach to molecular weight

determination. Using the results, and the fact that the λ_{max} values of the PPP-OPSO₃ π - π^* absorption ranged 339-342 nm, it is likely that minimum X_n can be about 40. The results in Table 3-4 are based on the assumption that each polymer chain has two *t*-butyl groups and the extent of conversion is 100% complete ($p=1$). However, if $p < 1$, each polymer chain may not have two *t*-butyl groups on its both ends. In addition, the possibility exists that the polymer chain ends are not properly capped as hydrolysis of the boronic acid group may occur. These possibilities may cause erroneously high values to be determined and the molecular weight of PPP-OPSO₃ remains inconclusive. However, the endcapping methodology proved its approach possible for the molecular weight calculation of water-soluble PPPs.

3-2-6 Photoluminescence and Electroluminescence Properties of Self-assembled Films based on PPP-OPSO₃

In the fluorescence study, PPP-OPSO₃ polymers proved their possibility as potential blue emitters. PPP-OPSO₃ was made into self-assembled films with a variety of polycations such as polyethyleneimine (PEI). Each of these systems show solid state fluorescence. Among these systems, the PPP-OPSO₃/PEI system was fully characterized. This work was carried out by M. Rubner group of the Massachusetts Institute of Technology.

PPP-OPSO₃/PEI multi-layer films were coated on ITO substrates. Aqueous solutions of polycation (PEI) and polyanion (PPP-OPSO₃) were prepared. Polycation followed by polyanion was coated, rinsing with water in between each step to remove any residual polymer. By repeating this, a thin film with a desired thickness was built up.

Absorbance and photoluminescence properties for the PPP-OPSO₃/PEI self-assembled films were determined. As shown in Figure 3-17, the

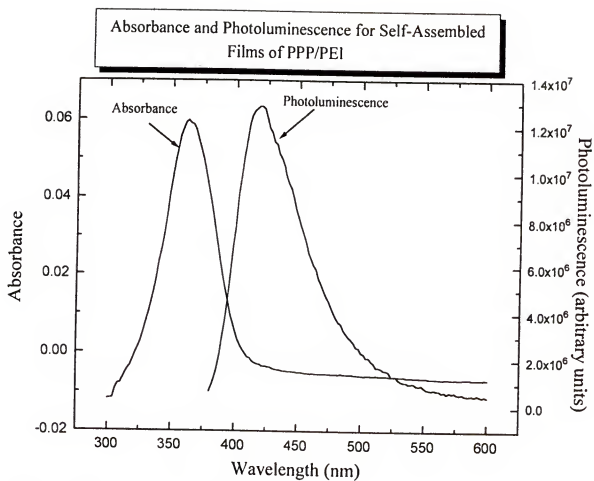


Figure 3-17 Absorbance and photoluminescence spectra for PPP-OPSO₃/PEI self-assembled film.

photoluminescence was measured at ~ 420 nm as was observed for PPP-OPSO₃ alone in aqueous solution.

Aluminum electrodes were deposited by vacuum evaporation of Al on the top of the PPP-OPSO₃/PEI film and Au wires connected to the Al and ITO electrode to create an electroluminescent device (Figure 3-18).

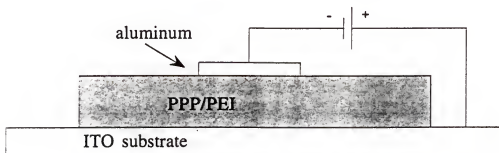


Figure 3-18 ITO/(PPP-OPSO₃/PEI)/Al type electroluminescence device.

Finally, voltage was applied from 0 V to 15 V in 1 V increment to induce charge carriers at the interface. Emitted light was detected as a function of the applied voltage change. Blue light began to be emitted when the applied voltage scaled 13 V and maximum light intensity was measured at 15 V as shown in Figure 3-19.

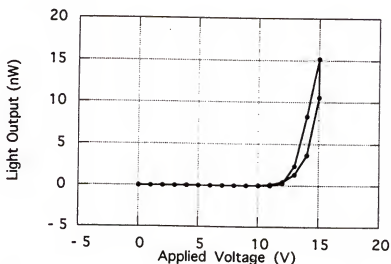


Figure 3-19 Light intensity change according to the applied voltage change on PPP-OPSO₃/PEI self-assembled film.

3-3 Experimental

3-3-1 Material Handling and Purification

1,4-Dibromobenzene was used as received. Fresh Mg turnings were prepared by crushing Mg pellets in a mortar with a pestle before use. Diboronic acid monomers, 1,4-benzenediboronic acid, and 4,4'-biphenylboronic acid, were purified by precipitation from water. The purified 1,4-benzenediboronic acid was dried *in vacuo* at 60 °C in order to prevent polymeric boronic anhydride formation⁶⁵ and stored in a drybox.

THF was dried over sodium/benzophenone before use. CH₂Cl₂ was dried from calcium hydride before use. Anhydrous conditions are important for the methyl cleavage reactions of boron tribromide to be studied.

4,4'-Biphenylboronic acid is insoluble in water and does not form crystals in any organic solvents.⁷³ Direct conversion of boronic acids to boronic esters using terminal diols was successful in obtaining monomers with sufficient purity for polycondensation reactions. The boronic ester monomer was stored in a desiccator.

The exposure of the reaction to air caused a color impurity for 2,5-dibromohydroquinone. The reaction of 2,5-dibromohydroquinone with NaOH in ethanol was very sensitive to oxygen. Once the reaction is exposed to air, the reaction turns brown causing a critical color impurity that cannot readily be removed. The 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene always contains water because the sulfonate groups are hygroscopic. It was dried in vacuum oven over 100 °C and then stored in a drybox.

The water-soluble Pd(0) catalyst is very sensitive to air. Once exposed to air, the catalyst changes color from bright yellow to red immediately. The Pd(0) catalyst synthesis was carried out entirely under inert conditions. It was also found that the Pd(0) catalyst slowly changes its color under exposure to light.

Therefore, the final product was transferred into a dry box and stored in a light-tight box.

In order to obtain a high degree of polymerization in polycondensation reaction, exact stoichiometric balances between the two different types of monomers are important. The monomers were stored in a drybox and each monomer was weighed up to 0.001 ± 0.0005 g for the best stoichiometric balance to obtain a high degree of polymerization. The glassware used was dried in an oven and immediately brought into the drybox in order to limit exposure to water. The reaction medium and monomers were deaerated to keep the catalyst reactivity as high as possible. The monomer-containing glassware was purged with argon for 30 min. before solvent addition. A mixture of 70% aqueous base with 30% DMF was also deaerated for one hour before use and transferred into a flask via canula.

3-3-2 General Characterization Methods Used

Dialysis membranes with a 3,500 g/mol cut-off were used for the purification of polymer products to remove NaHCO_3 , Na_2CO_3 , DMF, acetone, and some possible small molecules by products after the polymer precipitation from acetone. For the polymer samples with low molecular weights (ca. 1,000 to 3,000 g/mol), membranes with a 500 g/mol cut-off range were used. Initially, the dialysis membrane was soaked in water. Careful handling of the membrane is necessary to prevent the tube from leaking. Deionized water was used for dialysis as well as for the synthesis of the polymers. Reagent grade acetone was used for the precipitation of the products and purified by filtration before use in order to remove any possible particle impurities.

NMR spectra were obtained on Varian VXR-300 and Oxford Gemini-300 spectrometers. The intermediate products include a small amount of isomers,

side products, or impurities that are critical for monomer synthesis. CDCl_3 , $\text{DMSO}-d_6$, and D_2O were used as solvents for NMR spectra of the above samples. Polymer products were only soluble in D_2O . For a precise NMR characterization of sulfo-containing products, ampule-sealed D_2O was used as solvent.

TGA for water soluble PPP derivatives was carried out under nitrogen using a TA-2950 thermogravimetric analyzer system. For the analysis, 3 to 14 mg samples were used and the heating rate was $10\text{ }^\circ\text{C}/\text{min}$. All samples were dried prior to the period of temperature increase. The weight loss was reset to 100 % at the drying temperature indicating no weight change after water removal.

Elemental analysis was carried out for the synthesized products including monomers. The sulfur content in polymer products was carefully monitored through the analysis. This analysis was done by Robertson Microлит Laboratories, Inc. Madison, New Jersey showing good analysis results for carbon, hydrogen, and sodium.

A Varian Cary 5E UV-Vis spectrophotometer was used to measure absorption bands of the water-soluble PPPs. Deionized water was used as a solvent and the detection ranged from 200 to 800 nm. The λ_{max} values before and after dialysis were measured with a resolution limit of 1 nm. There was no significant λ_{max} change for the $\pi\text{-}\pi^*$ absorption, but some peak intensity change before and after dialysis.

A Spex 1680 0.22m Double Spectrometer was used to measure the fluorescence of the PPPs. Dilute samples ($\sim 10^{-4}\text{ mol/L}$) were prepared, diluted further if necessary due to the strong intensity of fluorescent light emitted. The samples were excited at 350 nm and the detection ranged from 370 to 700 nm.

The GPC system combined a Waters 6000A pump, a Waters ultra-hydrogel linear mixed bed column, and a 440 fixed wavelength detector, to measure molecular weights of the synthesized polymers.

3-3-3 Monomer Syntheses

3-3-3-1 Synthesis of 1,4-benzenediboronic acid⁷³

Synthesis of 1,4-benzenebis(dimethylborate) (1)

In a flame-dried 500 ml round bottom flask were added 9.7 g of Mg turning (0.40 mol), 100 ml of dry THF, and a small iodine chip, under argon. The mixture was stirred until iodine color disappeared. Subsequently a solution of 23.6 g of 1,4-dibromobenzene (Aldrich Chemical Co.) (0.10 mol) mixed with 150 ml of THF was added dropwise for 30 min. The mixture was refluxed 12 hours. White-colored Grignard product precipitated out from THF solution. The precipitate was cooled at 0 °C. To the mixture was slowly added 24 ml of trimethylborate (Aldrich Chemical Co.) (0.22 mol) from a dropping funnel. Greenish white powder, 1,4-benzenebis-(dimethylborate) swollen in THF was used without separation from solution.

Synthesis of 1,4-benzenediboronic acid (2)

To a stirred solution of 25 ml of concentrated sulfuric acid mixed with 100 ml of water was added 1,4-benzenebis(dimethylborate) swollen in THF at 0 °C. The solution was stirred vigorously for 30 min. The organic layer separated from water/THF solution was extracted with ether. Crude 1,4-benzenediboronic acid was collected and doubly recrystallized from boiling water. Colorless crystals were collected by filtration and dried *in vacuo* at 60 °C for 12 hours, yielding 5.62 g (33.6 %). ¹H-NMR (DMSO-*d*₆): δ 7.73 (s, 4H). ¹³C-NMR (DMSO-*d*₆): δ 133.04.

3-3-3-2 Synthesis of 4,4'-biphenyldiboronic acid-(2,2'-dimethyl)propyldiester⁷³

Synthesis of 4,4'-biphenylbis(dimethylborate) (3)

In a flame-dried 500 ml round bottom flask were added 4.86 g of Mg turning (0.20 mol), 150 ml of dry THF, and a small iodine chip, under argon. The mixture was stirred until iodine color disappeared. And then a solution of 24.96 g of 4,4'-dibromobiphenyl (Aldrich Chemical Co.) (0.08 mol) mixed with 150 ml of THF was added dropwise for 30 min. The mixture was refluxed for 48 hours. White-colored Grignard product precipitated out from THF solution. The precipitate was cooled at 0 °C. To the mixture was slowly added 24 ml of trimethylborate (Aldrich Chemical Co.) (0.22 mol) from a dropping funnel. Greenish white powder, 1,4-benzenebis-(dimethylborate) (1) swollen in THF was used without separation from solution.

Synthesis of 4,4'-biphenyldiboronic acid (4)

To a stirred solution of 25 ml of concentrated sulfuric acid mixed with 100 ml of water was added 4,4'-biphenylbis(dimethylborate) (5) swollen in THF at 0 °C. The solution was stirred vigorously for 30 min. The organic layer was separated from water/THF solution and then extracted with ether. Crude 4,4'-biphenyldiboronic acid was collected. The yellowish white crude diboronic acid was converted to diboronic acid sodium salt using aqueous 2 M NaOH. Filtrate was collected and reacidified using aqueous 2 M HCl. White powder was collected by filtration and dried *in vacuo* at 60 °C for 12 hours, yielding 1.21 g (6.25 %). ¹H-NMR (DMSO-*d*₆): δ 7.74(d, 4H), 7.98 (d, 4H), 8.15 (s, 4H). (some impurity included)

Synthesis of 4,4'-biphenyldiboronic acid-(2,2'-dimethyl)propylester (5)

To a 100 ml round bottom flask equipped with Dean-Stark were added 35 ml of toluene and 25 ml of DMSO. To the solution were added 1.21 g of 4,4'-biphenyldiboronic acid (0.005 mol) and 20.8 g of 2,2'-dimethyl-1,3-propanediol

(Aldrich Chemical Co.) (0.20 mol). The solution was refluxed at 110 °C for 12 hours and then cooled at 0 °C. The solution volume was reduced by evaporation and 100 ml of EtOH was added. The mixture was stirred for 30 min. White crystals were collected by filtration and washed with EtOH. Final product (*Z*) was dried *in vacuo* at 60 °C for 12 hours, yielding 1.85 g (97.1 %). mp 249-251 °C (lit.⁶⁵ mp 250 °C); ¹H-NMR (DMSO-*d*₆) δ 1.03 (s, 6H), 7.63 (d, 4H, *J*=9.0 Hz), 7.88 (d, 4H, *J*=9.0 Hz); ¹³C-NMR (DMSO-*d*₆) δ 21.91, 31.90, 76.59, 126.35, 134.31, 143.24.

3-3-3-3 Synthesis of 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene Synthesis of 1,4-dibromo-2,5-dimethoxybenzene (6)

In a 500 ml round bottom flask equipped with water condenser were added 13.8 g of 1,4-dimethoxybenzene (Aldrich Chemical Co.) (0.10 mol) and 200 ml of CCl₄ under argon. The mixture was stirred until solid disappeared. Into the solution was added dropwise 12.4 ml of bromine (Aldrich Chemical Co.) (0.24 mol) mixed with 80 ml of CCl₄ for 30 min. The mixture was stirred for 12 hours. Released HBr gas was collected in saturated aqueous NaOH. White-colored product precipitated out from the solution. The precipitate was collected by filtration and washed with cold ethanol. The filtrate was neutralized by adding aqueous 5 M K₂CO₃ with vigorous stirring until solution turned colorless. The CCl₄ solution was separated and recovered using rotovap. Crude product mixed with a small amount of monobrominated product was recrystallized from boiling ethanol. Combined pure 1,4-dibromo-2,5-dimethoxybenzene yielded 25.6 g (86.5 %). ¹H-NMR (CDCl₃) δ 3.84 (s, 6H), 7.10 (s, 2H); ¹³C-NMR (CDCl₃) δ 57.02, 110.57, 117.27, 150.60.

Synthesis of 1,4-dibromohydroquinone (7)

Into a 500 ml round bottom flask equipped with water condenser were added 13.2 g of 1,4-dibromo-2,5-dimethoxybenzene and 150 ml of dry

dichloromethane under argon. The mixture was stirred until solid disappeared. Into the solution was added 1.0 M boron tribromide in 100 ml of CH_2Cl_2 (Aldrich Chemical Co.) dropwise. The reaction was refluxed at 45 °C for 12 hours and then cooled at room temperature. The solution was slowly poured into ice-water solution at 0 °C. The solution was stirred vigorously for 30 min. Off-white precipitate was separated by filtration and washed with water. Pure 1,4-bromohydroquinone was collected and dried *in vacuo* at 60 °C for 12 hours, yielding 9.45 g (78.3 %). The product was used without further purification. mp 189-191 °C; $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ 7.07 (s, 2H), 9.82 (s, 2H); $^{13}\text{C-NMR}$ ($\text{DMSO}-d_6$) δ 108.43, 120.97, 147.60.

Synthesis of 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene (8)

In a 500 ml round bottom flask equipped with water condenser were added 5.36 g of 1,4-dibromohydroquinone (0.020 mol) and 100 ml of anhydrous EtOH under argon. The mixture was stirred until solid disappeared. In 100 ml of EtOH was dissolved 1.70 g of NaOH (0.044 mol) for 1 hour. The NaOH in EtOH was added dropwise and stirred for 1 hour. Yellow-colored solution turned orange-red. Into the solution was added 5.39 g of 1,3-propanesultone (Aldrich Chemical Co.) (0.042 mol) in 50 ml of EtOH. The reaction was vigorously stirred for 12 hours. White-colored product precipitated out from the solution. The product was collected by filtration and washed with EtOH. Purified final product was obtained by doubly recrystallization from water. Pure 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene yielded 5.68 g (51.2 %) after drying *in vacuo* at 100 °C for 12 hours. $^1\text{H-NMR}$ (D_2O) δ 2.20 (t, 4H, $J=6.9$ Hz), 3.13 (qt, 4H, $J=2.4$ Hz), 4.10 (d, 4H, $J=6.3$ Hz), 7.21 (s, 2H); $^{13}\text{C-NMR}$ (D_2O) δ 24.62, 48.22, 69.37, 111.36, 119.56, 149.76.

3-3-4 Synthesis of Tris(diphenylphosphinobenzene-*m*-sulfonic acid) palladium(0) Sodium Salt Catalyst⁵⁰

Synthesis of diphenylphosphinobenzene-*m*-sulfonic acid sodium salt (9)

Into a 100 ml round bottom flask filled with 30 ml of fuming sulfuric acid (Aldrich Chemical Co.) was slowly added 10 g of triphenylphosphine (Aldrich Chemical Co.) (0.038 mol) at 0 °C. The mixture was heated at 50 °C for 20 min. and then at 60 °C. Test aliquot was taken from the solution every 10 min. and put into test tube filled with 3 ml of water. The reaction was stopped when the test aliquot did not show any precipitate. The solution was quenched in 200 ml of cold water and then neutralized by saturated aqueous NaOH. Neutral point was detected using pH paper. White shining crystals were collected by filtration and recrystallized from water. Final product was dried *in vacuo* at 60 °C for 12 hours yielding 8.6 g (63.2 %). ¹H-NMR (DMSO-*d*₆) δ 7.19 (t, 1H, *J*=6.0 Hz), 7.26 (m, 4H), 7.38 (t, 1H, *J*=6.0 Hz), 7.41(m, 6H), 7.61 (qt, 2H, *J*=6.2 Hz).

Synthesis of tris(diphenylphosphinobenzene-*m*-sulfonic acid)palladium(0) sodium salt (10)

Into 100 ml 3 neck round bottom flask equipped with medium glass filter in one neck was charged 10 ml of DMSO distilled from CaH₂. To the solution were added 3.00 g of diphenylphosphinobenzene-*m*-sulfonic acid sodium salt (8.25 mmol) and 0.44 g of PdCl₂ (2.25 mmol) under argon purge. The mixture was purged with argon for 30 min. and then heated at 100 °C for 30 min. To the solution was 0.5 ml of hydrazine (Aldrich Chemical Co.) slowly. The reaction was kept heating for 15 min. and cooled at room temperature. Bright yellow solid precipitated out by adding 50 ml of CH₂Cl₂ and then collected by filtration under inert condition. The product was *in situ* recrystallized from 30 ml of deaerated EtOH and collected by filtration after lowering temperature at 0 °C. Final product was dried *in vacuo* at room temperature for 12 hours under argon.

purge and transferred into drybox yielding max. 2.14 g (74.0 %). $^1\text{H-NMR}$ (CD_3OD) δ 7.08 (m, 15H), 7.22 (m, 18H), 7.35 (t, 3H, $J=8.6$ Hz), 7.69(m, 6H), 7.61 (qt, 6H, $J=6.2$ Hz).

3-3-5 Model Compound Synthesis

Synthesis of 2,5-diphenyl-1,4-(2-sulfonatopropoxy)benzene sodium salt (11)

To a 250 ml three neck flask fitted with water condenser were added 0.834 g of 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene (1.5 mmol) and 0.366 g of 1,4-benzeneboronic acid (3.0 mmol). Into the mixture, 0.052 g of water-soluble Pd(0) complex (3 mol%), or 0.010 g of $\text{Pd}(\text{OAc})_2$ (Aldrich Chemical Co.) (3 mol%) was transferred in drybox. The contents were purged under argon for 30 min. Subsequently 100 ml of 70 % aqueous 0.2 M Na_2CO_3 /30 % DMF mixture was transferred via canula after deaeration for 1 hour. The reaction was heated at 85 $^\circ\text{C}$ for 12 hours for water-soluble Pd(0) complex (6 hours for $\text{Pd}(\text{OAc})_2$). The mixture turned black as Pd(0) particles were liberated. The filtrate was collected and then poured into 500 ml of acetone. Off-white precipitate that formed was collected by filtration and recrystallized from water. White powder was collected by filtration and dried *in vacuo* at 100 $^\circ\text{C}$ overnight, yielding max. 0.46 g (55.7 %) $^1\text{H-NMR}$ (D_2O) δ 1.86 (t, 4H, $J=5.1$ Hz), 2.69 (q, 4H, $J=2.4$ Hz), 3.36 (t, 4H, $J=6.0$ Hz), 6.70 (s, 2H), 7.29-7.32 (m, 4H), 7.42-7.44 (m, 6H); $^{13}\text{C-NMR}$ (D_2O) δ 25.56, 49.26, 68.85, 117.28, 128.77, 129.48, 130.44, 131.73, 138.36, 150.54. Anal. calcd for $\text{C}_{24}\text{H}_{24}\text{O}_8\text{S}_2\text{Na}_2 \cdot 1.5\text{H}_2\text{O}$: C, 50.34; H, 4.65; S, 10.53; Na, 7.84. Found: C, 49.91; H, 4.68; S, 11.09; Na, 7.97, Br, 0.08.

3-3-6 Polymer Syntheses

Synthesis of PPP-OPSO₃ (12)

Into a 100 ml three neck flask, equipped with mechanical stirrer were added 0.834 g of 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene (1.5 mmol) and 0.249 g of 1,4-benzenediboronic acid (1.5 mmol) under an argon. Into the mixture, 0.052 g of water-soluble Pd(0) complex (3 mol%), or 0.010 g of Pd(OAc)₂ (3 mol%) was transferred in drybox. The contents were purged under argon for 30 min. And then 100 ml of 70 % aqueous buffer (pH 8.0, 10.0, or 12.0)/ 30 % DMF mixture was transferred via canula after deaeration for 1 hour. The reaction was heated at 85-90 °C for 24 hours. The reaction turned black as Pd(0) particles were liberated. The tan-violet filtrate was collected by filtration and then poured into 1 L of acetone. Crude polymer was precipitated into acetone and redissolved in deionized water. The crude polymer was dialyzed using a membrane with a 3,500 g/mol cut-off for 3 days. The final product, a tan-violet colored polymer, was obtained after drying *in vacuo* at 110°C for 24 hours, yielding max. 0.280 g (39.5 %) after dialysis. ¹H-NMR (D₂O) δ all broad peaks 2.10, 2.98, 3.92, 7.04, 7.63; ¹³C-NMR (D₂O) δ 25.36, 48.90, 68.51(broad), 117.02, 130.25, 137.34, 150.44. Anal. calcd for [C₁₈H₁₈O₈S₂Na₂•2.5H₂O]_x: C, 41.79; H, 4.65; S, 12.39; Na, 8.89. Found: C, 43.04; H, 4.62; S, 11.21; Na, 7.92, Br, 0.15.

Synthesis of PPBP-OPSO₃ (13)

Into a 100 ml three neck flask, equipped with mechanical stirrer were added 0.834 g of 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene (1.5 mmol) and 0.567 g of 4,4'-biphenyldiboronic acid (2,2'-dimethyl)propyldiester (1.5 mmol) under an argon. Into the mixture, 0.052 g of water-soluble Pd(0) complex (3 mol%) was transferred drybox. The contents were purged under argon for 30 min. And then 100 ml of 70 % aqueous buffer (pH 8.0, 10.0, 12.0)/ 30 % DMF

mixture was transferred via canula after deaeration for 1 hour. The reaction was heated at 85-90 °C for 24 hours. The mixture turned black as Pd(0) particles were liberated. The tan-violet filtrate was collected by filtration and then poured into 1000 ml of acetone. Crude polymer was precipitated into acetone and redissolved in deionized water. The polymer was dialyzed using a membrane with a 3,500 g/mol cut-off for 3 days. The final product, a tan-violet colored polymer, was obtained after drying *in vacuo* at 110 °C for 24 hours, yielding max. 0.410 g (50.0 %) after dialysis. ¹H-NMR (D₂O) δ all broad peaks 2.12, 2.96, 3.93, 7.07, 7.61; ¹³C-NMR (D₂O) δ 25.39, 48.90, 68.10(broad), 116.98, 130.08, 137.42, 150.34. Anal. calcd for [C₂₄H₂₂O₈S₂Na₂•5H₂O]_x: C, 45.14; H, 3.47; S, 10.04; Na, 7.20. Found: C, 46.36; H, 4.83; S, 9.15; Na, 6.36, Br, 0.30.

3-3-7 TBPPP-OPSO₃ syntheses

Synthesis of 4-*t*-butylbenzeneboronic acid (14)⁷³

Into a 250 ml three neck flask, equipped with mechanical stirrer was transferred 10.0 ml of 4-*t*-butylphenylmagnesium bromide in ether (0.1 mol eq.) via canula under an argon. Into the mixture, 3.5 ml, of trimethylborate (0.025 mol) in dry ether 10 ml was added dropwise. The reaction was stirred at room temperature for 2 hours. Into the mixture was added 100 ml of cold 2 M HCl. Organic layer was collected by extraction with 300 ml of ether. Crude product was collected after the evaporation of ether. White crystals were obtained after recrystallization from water. The final product was dried *in vacuo* at 60 °C for 24 hours, yielding max. 1.48 g (41.6 %) after double recrystallization. ¹H-NMR (DMSO-*d*₆) δ 1.34 (s, 9H), 7.41 (d, 2H, J=8.1 Hz), 7.55 (d, 2H, J=8.1 Hz), 7.99 (s, 2H); ¹³C-NMR (DMSO-*d*₆) δ 32.04, 35.36, 125.07, 135.01, 153.43.

Synthesis of TBPPP-OPSO₃ (15)

Into a 100 ml three neck flask, equipped with mechanical stirrer were added 0.834 g of 1,4-dibromo-2,5-di(3-sulfonatopropoxy)benzene (1.5 mmol) and 0.249 g of 1,4-benzenediboronic acid (1.5 mmol) under an argon. Into the mixture, the calculated amount of 4-*t*-butylbenzeneboronic acid according to the desired stoichiometric imbalance for molecular weight control. Subsequently 0.010 g of Pd(OAc)₂ (3 mol%) was transferred. The contents were purged under argon for 30 min. And then 100 ml of 70 % aqueous 0.2 M Na₂CO₃ / 30 % DMF mixture was transferred via canula after deaeration for 1 hour. The reaction was heated at 85-90 °C for 24 hours. The mixture turned black as Pd(0) particles were liberated. The tan-violet filtrate was collected by filtration and then poured into 1000 ml of acetone. Crude polymer was precipitated into acetone and redissolved in deionized water. The polymer was dialyzed using a membrane with a 500 or 3,500 g/mol cut-off for 3 days according to the expected molecular weight. The final product, a tan-brown to tan-violet colored polymers, were obtained after drying *in vacuo* at 110°C for 24 hours, yielding max. 0.249 g (35.2 %) after dialysis. ¹H-NMR (D₂O) δ all broad peaks 1.21, 2.06, 2.98, 3.97, 7.04, 7.57 .

3-4 Conclusions

New water-soluble PPP derivatives, PPP-OPSO₃, and PPBP-OPSO₃ have been synthesized and characterized. The incorporation of sulfonatopropoxy groups onto the PPP backbone induces water-solubility. PPP-OPSO₃ and PPBP-OPSO₃ dissolved well in water. Two different Pd catalysts, a water-soluble Pd(0) complex, and Pd(OAc)₂ were used to obtain high polymer in a different pHs (8.0, 10.0, and 12.0). Degrees of polymerization were monitored using λ_{max} values of π-π* absorption. An endcapping method

was employed to determine the approximate molecular weight of PPP-OPSO₃. The endcapping method results are inconclusive, but the methodology showed a plausible approach to the number average molecular weight calculation of PPP-OPSO₃. TGA results of all polymers show that the water-soluble PPPs are thermally stable with onset temperatures for degradation over 300 °C under nitrogen. PPP-OPSO₃ and PPBP-OPSO₃ are fluorescent in both aqueous solution and the solid state. Multi-layer films assembled with polycations such as PEI are electroluminescent materials, potentially useful for blue-emitting devices.

CHAPTER 4 OVERALL CONCLUSIONS AND DIRECTIONS OF FUTURE RESEARCH

Polyelectrolytes with aromatic backbones, specifically sulfonated polybenzothiazoles (PBTs), and sulfonatopropoxy-substituted poly(*p*-phenylenes) (PPPs), have been synthesized and characterized.

Structural analyses for sulfo PBTs (*p*-sulfo PBT, *m*-sulfo PBT, and *m*-disulfo PBT) confirm the synthesis of *p*-sulfo PBT and *m*-disulfo PBT, but suggest that the sulfo groups of *m*-sulfo PBT are cleaved during the polymerization. The addition of sulfo groups onto PBT enhances solubility in organic solvents such as DMSO. *m*-Disulfo PBT is water soluble at room temperature. A mixed solvent system study indicates an MSA/CH₂Cl₂ mixture to be the most aggressive of solvents evaluated at room temperature. *p*-Sulfo PBT exhibits birefringence in DMSO, as well as in a H₂O/DMSO mixture, indicating the material to be lyotropic.

Water soluble poly(*p*-phenylene) derivatives, PPP-OPSO₃ and PPBP-OPSO₃, have been synthesized through Suzuki coupling reaction using a water soluble Pd(0) catalyst or Pd(OAc)₂. The incorporation of sulfonatopropoxy groups onto PPP backbones induces charge carrier stability as well as water-solubility. The pH dependence study of the coupling reactions indicates that high degrees of polymerization can be attained at high pH. An endcapping method to determine the molecular weight of PPP-OPSO₃ was attempted, but the results are inconclusive. The methodology does provide its plausible approach to molecular weight estimation and should be more thoroughly examined in the future.

PPP-OPSO₃ and PPBP-OPSO₃ are fluorescent in both aqueous solution and solid state, being blue emitters. PPP-OPSO₃/polyethyleneimine (PEI) multi-layers show blue photoluminescence and electroluminescence. Further luminescence studies for these materials are in progress and focused towards device fabrication. Different multi-layer films such as PPP-OPSO₃/PPV precursor (PPV-p) are under study. Future work should be extended to the luminescence and fluorescence properties of a broad family of conjugated polyelectrolytes. Viscosity measurements will be carried out to complete the structural characterization of PPP-OPSO₃.

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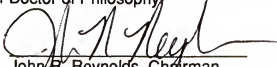
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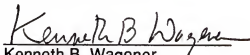
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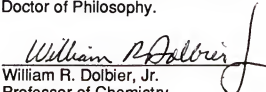
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